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THE EFFECT OF TEMPERATURE, OF COLLOIDAL FERRIC HYDRATE, AND OF A MAGNETIC FIELD ON THE HYDROLYSIS OF FERRIC CHLORIDE.

By H. M. Goodwin and Frederick W. Grover.

THE present investigation is a continuation of one published by one of us[1] in 1896, on the changes which take place in a neutral ferric chloride solution when greatly diluted. Such solutions when first prepared of a concentration of about 0.001 normal are nearly colorless but rapidly change to a deep reddish brown, and this gradual color reaction is accompanied by a corresponding increase in the electrical conductivity of the solution. In the paper cited, the hydrolytic reaction giving rise to this phenomena was studied by following the changes in the conductivity of the solution, and the main results of the investigation may be summarized as follows :

1. The electrical conductivity of dilute ferric chloride solutions increases with the time.

2. The rate of increase, increases very rapidly with the dilution.

3. The increase in conductivity does not begin at once on dilution, but only after the lapse of a certain time.

4. This initial lag or time required to start the reaction increases rapidly with the concentration, being for example, one minute for a

[1] Goodwin, Phys. Rev., 9, 251, 1896.

0.0006 normal solution, 15 minutes for a 0.0012 normal solution and 45 minutes for a 0.0024 normal solution.

5. The time required for a solution to reach a state of equilibrium increases enormously with the dilution,—a 0.0001 normal solution requiring for example only three hours while a solution six times as strong requires over a week.

6. The hydrolytic dissociation was computed and found to be very large in dilute solutions.

The explanation offered for this peculiar behavior was the gradual formation of Graham's colloidal ferric hydrate from the electrolytically hydrolyzed ferric chloride, according to the reaction

$$x\,\overset{+}{\mathrm{Fe}}\overset{+}{\mathrm{O}}\mathrm{H} + x\,2\overset{-}{\mathrm{O}}\mathrm{H} = (\mathrm{FeO_3H_3})x.$$

The formation of colloidal hydrate accounted for the color changes observed, while the removal of the $\overset{+}{\mathrm{Fe}}\overset{+}{\mathrm{O}}\mathrm{H}$ ions from the solution displaced the hydrolytic equilibrium thus causing more chloride to be hydrolyzed with accompanying increase of conductivity. The initial lag observed in the reaction and the remarkable acceleration of its rate when once started was explained on the hypothesis that the rate of formation of the colloidal hydrate was dependent on the presence of a certain amount of the colloid itself, analogous to the rate of crystallization being a function of the number of crystallizing nuclei around which the crystals can form.

The present investigation was undertaken first to study the effect of temperature on the rate of the reaction, the former measurements all having been made at 25°; second to test the above hypothesis regarding the cause of the accelerated rate of the reaction after the lapse of a certain time; and third to see if any effect could be observed on the rate of the reaction of a strong magnetic field.

APPARATUS AND METHOD.

The conductivity measurements were made by the familiar Kohlrausch method. The solutions were diluted as in the previous investigation by adding with a pipette a few cubic centimeters of a strong solution of neutral ferric hydrate to a previously weighed amount of distilled water brought to the proper temperature of the

experiment. This water was contained in 250 cc. or 500 cc. thoroughly steamed wide necked glass bottles which served also as measuring cells. It was found very advantageous to use "plunge electrodes" in cells of this kind (Kohlrausch & Holborn's Leitvermögen der Electrolyte, p. 19) instead of the usual Arrhenius type previously employed. The considerable care and patience required in the preparation of these electrodes was more than compensated for by their absolute constancy and particularly the independence of their "constant" from the position of the electrodes in the bottle. Electrodes about one square centimeter in area platinized with a Lummer-Kurlbaum solution gave an excellent minimum for most dilutions investigated. The solutions were investigated at 0°, 15° and 25° C. The first temperature could of course be maintained indefinitely constant by a large ice bath packed in hair felt in which the bottles were completely immersed. A temperature of 15° C. was maintained constant to within 0.1° during the day and 0.2°–0.3° during the night by means of a large tank of water, insulated from outside temperature changes by being packed in a box with six inches of finely divided cork and covered with four inches of air felt. A temperature of 25° was maintained indefinitely constant to a few hundredths of a degree in the large 5x3x3 foot automatically regulated and electrically heated thermostat of the laboratory.

Solutions.

Ferric Chloride.—The stock ferric chloride solution used in the following experiments was made from a preparation of sublimed ferric chloride from Eimer and Amend. A quantity weighed from a weighing tube was made up to one gram-equivalent in a liter and then analyzed for chlorine. Three analyses gave an equivalent normality of 0.966, 1.001 and 0.999, the mean being 0.9987. This solution had an equivalent conductivity of 43.6 at 24.96° C. after standing about a week. This stock solution was then diluted ten or a hundred times for the secondary stock solutions used in the subsequent great solutions.

Graham's Colloidal Ferric Hydrate.—A solution of Graham's soluble colloidal hydrate was prepared by treating a saturated solution of pure (unsublimed) ferric chloride with ammonium carbonate

with constant stirring, until the light colored precipitate which formed just refused to dissolve on further stirring. The color of the solution rapidly turned to an intense garnet color. It was then subjected to dialysis for thirty-two days. The concentration of the resulting solution was determined by evaporating to dryness and igniting portions of 10 cc. each and weighing the ferric oxide. The mean of two determinations showed it to be 0.3085-equivalent normal with respect to $Fe(OH)_3$. It still contained some ammonium salts as shown by a slight visible volatilization on first heating and from the fact that the solution had a considerable conductivity which had it contained only colloidal hydrate should not be the case. At 18.1° its specific conductivity was 0.00304, which corresponds to that of an ammonium chloride solution about 0.02 normal.

EXPERIMENTAL RESULTS.

In the following Tables are tabulated the results obtained at 25°, 15.5°, and 0°, with solutions of the indicated concentrations, C always being expressed in *gram equivalents* in a litre. The conductivities are those observed at the indicated time intervals elapsing from the time of dilution. The values are expressed as equivalent conductivities in reciprocal Siemen's units for convenience of comparison with former measurements.

TABLE I.

$C = 0.000150$. $t = 24.92°$. *Diluted from* $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 40	295.3	37 25	363.6
2 35	310.2	58 50	364.8
4 25	323.1	1 28 45	366.9
6 15	326.8	2 1 15	366.9
7 30	328.3	.....	.....
14 35	350.9	20 19	364.8
18 35	353.0	21 21	364.8
27 35	358.7		

TABLE II.

$C = 0.0004545$. $t = 25.12°$. *Diluted from* $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 0	260.2	13 10	319.8
2 30	267.8	14 45	322.1
3 0	272.5	18 10	326.8
3 45	280.3	21 45	330.2
4 20	284.9	27 40	333.8
4 50	287.8	33 40	335.6
5 30	295.7	37 35	338.6
6 0	297.9	1 42 0	351.1
6 35	300.6	2 10 0	352.4
7 5	302.2	4 50 0	352.4
8 30	306.6	.....	.....
10 40	315.5	27	351.
12 15	318.7		

TABLE III.

$C = 0.000906$. $t = 25°.09$. *Diluted from* $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 40	214.6	12 30	277.0
3 20	223.5	15 0	283.3
3 55	229.1	21 0	294.8
4 40	236.8	24 30	300.1
5 30	242.5	32 15	309.3
1 20	252.2	45 30	318.7
6 50	255.6	59 30	326.4
7 40	259.4	1 15 30	331.7
8 20	263.0	1 39 30	337.7
9 40	266.8	2 51 0	344.6
10 30	270.7		
11 0	272.4		
12 0	275.4		

TABLE IV.

$C = 0.001335$. $t = 25°.04$. *Diluted from* $C = 0.0909$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent Conductivity.
2 0	200.6	23 45	274.2
2 55	209.1	27 45	279.9
3 25	212.6	44 0	294.0
4 25	222.9	50 0	297.7
5 15	228.7	1 30 0	316.6
6 45	234.5	2 6 0	325.1
9 45	246.3	2 24 0	328.1
14 30	259.2	2 35 0	329.6
17 5	266.3		

TABLE V.

$C = 0.00360$. $t = 24°.96$. *Diluted from* $C = 0.999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 45	183.5	41 20	212.3
4 20	185.3	56 0	222.2
5 0	185.3	1 9 0	229.7
7 55	186.9	1 26 20	239.3
8 45	187.6	1 38 0	243.0
10 10	188.2	1 51 0	248.0
13 0	190.3	2 11 0	254.5
16 0	193.2	2 36 0	261.6
23 15	198.7	2 49 0	264.5
26 25	201.1	2 58 0	266.4
34 45	207.4	3 3	268.1

TABLE VI.

$C = 0.00750$. $t = 24.87°$. *Diluted from* $C = 0.999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
4 0	171.9	42	176.0
8 0	172.8	56	178.0
11 30	172.8	1 2	180.2
15 0	173.4	3 7	206.7
17 0	173.2	3 9	207.5
20 0	173.7	3 14	208.9
23 0	174.6	3 20	210.0
27 0	174.3	.....	
30 0	175.6	21	260.
35 0	175.3		

Table VII.

$C = 0.000150$. $t = 15°.5$. *Diluted from* $C = 0.0100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
3 15	249.3	18 20	281.7
4 15	255.3	19 45	283.6
5 0	259.0	26 10	287.1
6 45	264.1	51 0	292.8
8 50	269.6	1 1 0	294.7
10 10	273.7	1 31 0	296.5
11 40	274.8	2 6 0	297.7
12 10	276.0	.....	.....
14 10	279.3	18 23	301.6

Table VIII.

$C = 0.00033$. $t = 15°.4$. *Diluted from* $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 35	207.4	22 0	256.2
3 30	210.2	31 30	260.3
5 5	220.8	38 10	263.2
6 50	231.8	49 50	267.6
7 30	233.8	1 0 35	269.4
9 20	238.6	1 27 50	274.7
12 35	245.0	2 9 10	279.1
14 10	246.8	.....	.....
17 50	251.4	25 54	286.0

Table IX.

$C = 0.0004545$. $t = 15.9°$. *Diluted from* $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
3 40	182.2	25 40	233.3
4 25	186.6	31 0	238.7
5 20	191.1	1 0 35	256.1
6 40	197.2	1 19 20	262.0
7 55	201.5	1 38 0	268.3
10 25	209.4	1 49 0	270.9
13 55	217.4	1 55 0	272.2
16 40	221.9	.....	.....
21 35	228.7	19 28	301.9

TABLE X.

$C = 0.000909$. $t = 15.7°$. *Diluted from* $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 15	167.0	54 0	206.2
2 50	167.5	1 9 0	214.1
3 15	168.2	1 29 0	222.1
3 45	168.3	1 39 0	225.6
4 15	168.7	1 57 0	231.5
5 30	169.6	2 28 0	238.9
6 0	170.0	2 47 0	243.0
7 45	170.9	3 24 0	249.9
14 30	177.1	23 — —	298.3
25 45	187.1		
38 15	196.5	5 d. 23 h.	299.5

TABLE XI.

$C = 0.001335$. $t = 15°.5$. *Diluted from* $C = 0.100$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 0	167.8	1 13	188.6
2 50	168.0	1 43	203.3
5 35	168.9	2 13	212.4
10 10	170.0	2 52	222.4
14 20	170.8	22 49	285.9
27 50	175.8		
38 30	179.7	7 d. 20 h.	300.7

TABLE XII.

$C = 0.00500$. $t = 15°.6$. *Diluted from* $C = 0.999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
7	146.4	2 38	149.0
10	146.5	2 53	149.3
18	146.6	3 6	149.1
28	147.0	8 10	153.1
32	147.1	1 2 22	198.0
41	147.2	3 5 48	219.3
57	147.3	4 5 32	223.1
1 28	147.8	6 4	223.4

Solution colorless during first 8 hours.
" deep yellow after 1 day.

Table XIII.

$C = 0.00750$. $t = 15°.5$. *Diluted from* $C = 0.999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
4	139.5	21 58	140.0
1 41	140.8	3 1 51	178.1
1 52	140.8	4 0 59	188.9
2 3	141.0	6 0 31	199.1
4 2	140.4		

Solution colorless during first 21 hours.
" deep yellow after 3 days.
" slightly turbid after 4 days.
" very " " 6 "

Table XIV.

$C = 0.000150$. $t = 0°$. *Diluted from* $C = 0.00999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
4 0	122.6	3 11	171.7
6 30	129.1	4 14	174.6
8 0	131.1	6 4	178.4
10 0	135.0	6 54	178.9
14 40	140.5	7 28	179.8
26 0	145.4	24 44	183.0
1 24 0	162.8	3 d. 2 h.	183.0
2 37 0	170.6		

Table XV.

$C = 0.00033$. $t = 0°$. *Diluted from* $C = 0.00999$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 30	121.1	34 30	124.6
3 15	121.6	56 0	127.6
5 20	121.7	1 16 0	131.1
6 30	122.1	1 50 0	136.6
9 0	122.1	2 34 0	142.5
11 10	122.6	3 1 0	145.4
17 0	123.2	1 d. 20 h.	194.1
25 15	124.6	3 d. 40 m.	600.3

TABLE XVI.

$C = 0.0004545$. $t = 0°$. *Diluted from* $C = 0.090$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
6 0	113.9	6 8	130.8
7 0	114.3	6 53	135.5
7 30	114.7	7 10	137.0
9 0	115.3	7 36	138.4
12 0	116.1	d. h. m.	
23 0	117.3	1 3 30	167.6
1 26 0	123.2	1 4 14	168.6
3 11	121.1	1 6 13	169.5
4 4	125.9		

TABLE XVII.

$C = 0.000909$. $t = 0°$. *Diluted from* $C = 0.0999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
6	113.1	1 40	113.9
25	112.0	2 20	115.0
31	112.1	3 16	116.1
51	112.6	1 5 20	143.3
$C = 0.000909$.		*Diluted from* $C = 0.0909$.	
37	110.0	1 6 30	144.5
2 54	113.0	4 1 40	160.0
6 19	113.3	5 1 28	159.9
22 23	114.2		

TABLE XVIII.

$C = 0.001335$. $t = 0°$. *Diluted from* $C = 0.0999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
27	107.9	1 19 11	123.4
1 24	107.9	2 2 7	130.0
1 54	107.9	2 19 13	136.0
1 1 15	107.8	4 19 6	145.1
1 17 32	121.3	8 2 32	147.6

Solution deep yellow.

TABLE XIX.

$C = 0.00250$. $t = 0°$. *Diluted from* $C = 0.0999$.

Time elapsed. d. h. m.	Equivalent conductivity.	Time elapsed. d. h. m.	Equivalent conductivity.
32	101.4	5 1 23	106.7
2 0	99.9	6 1 53	112.6
3 1 19	99.7	6 21 18	117.8
3 22 20	101.2	10 — —	125.1
4 20 27	105.6	12 — —	128.5

DISCUSSION OF RESULTS.

The data in the preceding tables is represented graphically in the following plots (1, 2, 3 and 4). Considering first plot 1, con-

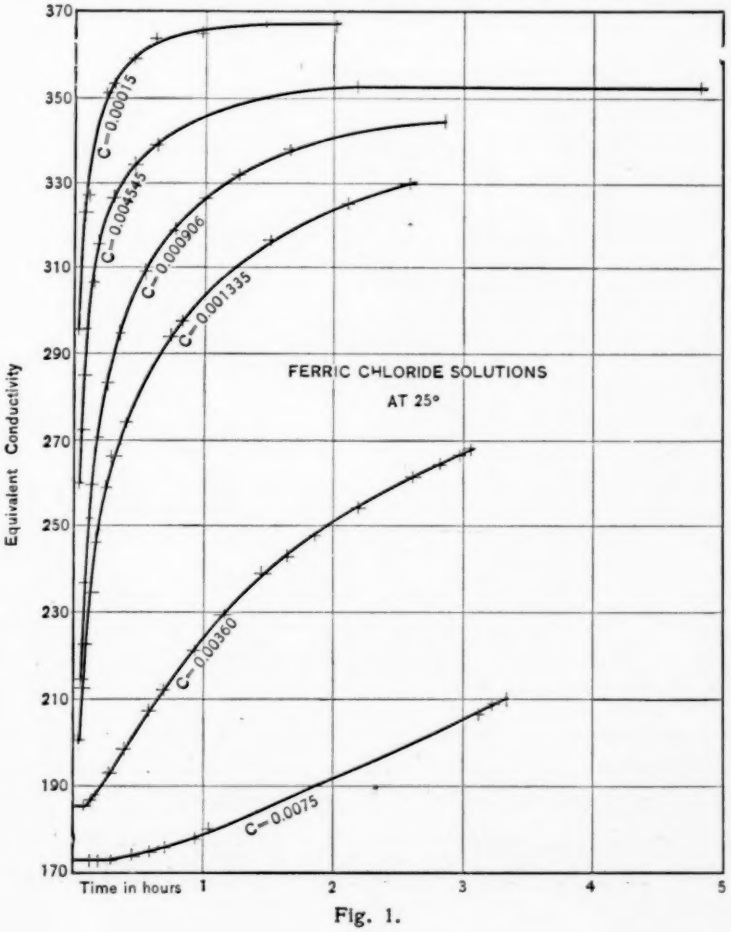

Fig. 1.

taining the results at 25°, we find that the earlier results at this temperature are in general well confirmed. The initial values for $t = 0$ and the form of the curves agree well with those previously obtained, but the initial lag in the present series is less than in the former. This may be due to the fact that in the former experi-

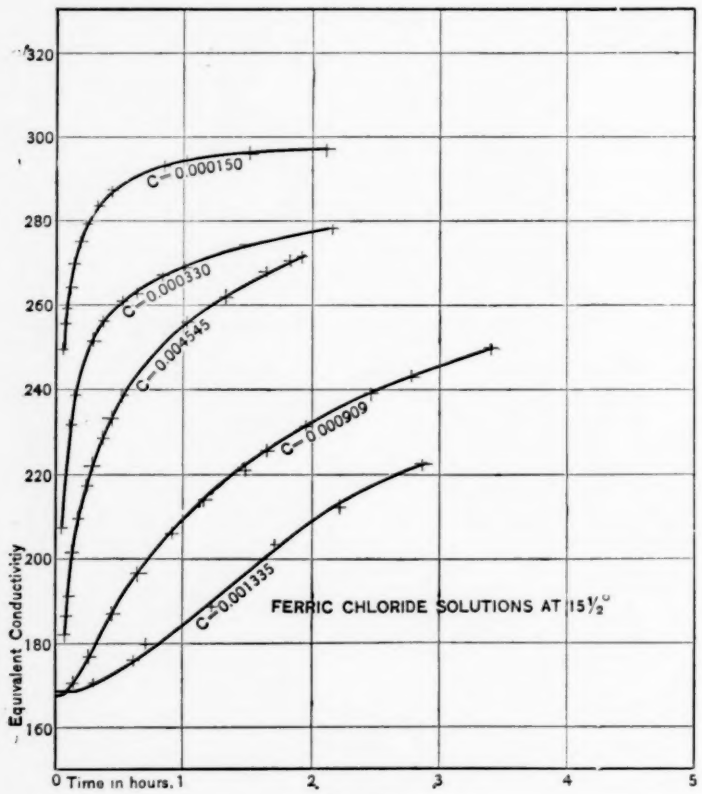

Fig. 2.

ments, the "stock" solution from which the dilutions were made, was three times as strong as the present "stock" solution. The "lag" is, however, unmistakable in the solution $C = 0.0075$.

On comparing plot 1 with plots 2, 3 and 4 the enormous effect of temperature on the reaction is at once evident. Whereas, the hour was a convenient unit for representing the data at 25°, the day must be used to represent the data at 0° and the more concentrated solutions at 15°. It is seen, as was expected, that lowering the

temperature diminishes the rate of the reaction, increases its initial lag, and the time required to reach equilibrium. The form of the curves for equal concentration thus flatten out with decreasing tem-

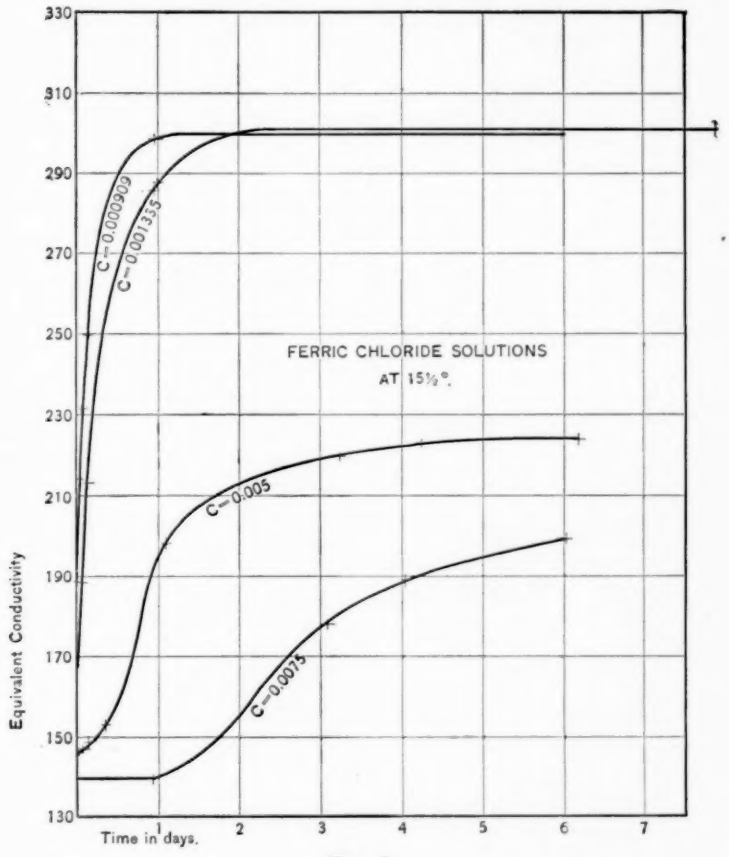

Fig. 3.

perature; the curves for the solutions at 25° approach in form, in fact almost coincide with, the curves for greater dilutions at lower temperatures. Thus compare:

at 25°	at 15°
$C = 0.0004545$	$C = 0.00015$
$C = 0.001335$	$C = 0.0004545$
$C = 0.00360$	$C = 0.000909$

A decrease of temperature of 10° from 25° has nearly the same effect on retarding the reaction as increasing its concentration about three times; lowering the temperature to 0° retards the reaction as much as increasing the concentration fifteen to twenty times.

It is interesting to note how the solution $C = 0.001335$, which exhibits no lag at 25°, does not change appreciably until after about five minutes at 15.5°, and does not change until after a day at 0°.

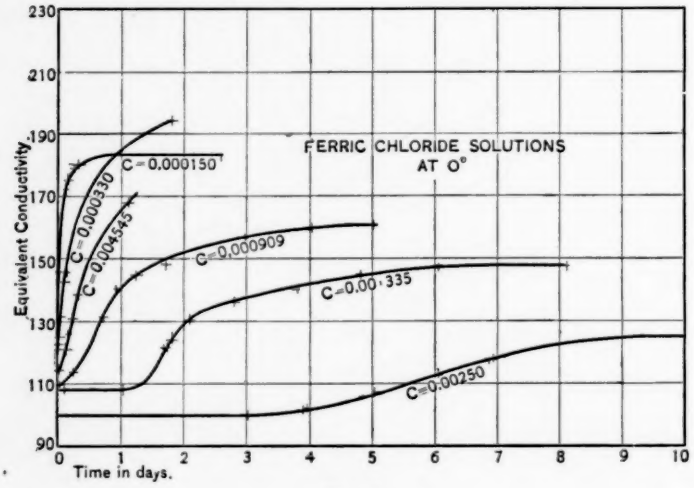

Fig. 4.

The solution $C = 0.0025$ remains unchanged at 0° until after four days, and it is probable that a solution of $C = 0.005$ which has a lag of a few hours at 15° would remain practically unchanged at 0°. The general expression for the rate of change as function of the temperature cannot, however, be determined from the data yet at hand.

In the course of the experiments a few observations were also made on the effect of temperature on the turbidity of ferric chloride solutions of certain concentrations when allowed to stand. This turbidity, which is probably due to the formation of oxychloride was found by Goodwin to be accompanied by a corresponding change in conductivity of the solutions and to have a "lag" dependent on the concentration of the solution.

Thus a 0.09 normal solution became turbid only after the lapse

of two weeks while a solution ten times as dilute became turbid in about a day. On the other hand, a solution 0.0057 normal remained perfectly clear even after two weeks thus showing that the precipitate was formed at 25° only within narrow limits of concentration.

In the present investigation, solutions of strengths 0.02, 0.01, 0.004 and 0.002 normal were found to remain perfectly clear for at least two weeks when kept in ice. A 0.0075 normal solution on the other hand, became very turbid at 25° in less than four days, slightly turbid in the same time at 15° (very turbid after six days), while it remained clear at 0°.

Lowering the temperature thus greatly tends to diminish the separation of oxychloride from the solution as well as to prevent the formation of colloidal hydrate.

II.

Effect of Colloidal Ferric Hydrate on the Reaction.

To test whether the hypothesis, previously advanced to account for the accelerated rate of the reaction when once started, was verified by experiment, various amounts of previously prepared Graham's colloidal ferric hydrate were added to dilute solutions of ferric chloride, and the change in conductivity then followed as in the previous experiments. A solution 0.0075- equivalent normal and a temperature of 25° were chosen, as the preceding experiments showed that at this temperature a solution of this strength had a marked initial lag of about 20 minutes. A known amount of best distilled water was weighed out in a 250 cc. bottle, brought to a temperature of 25°, and a known small amount of the colloidal ferric hydrate added with a pipette. The specific conductivity of this solution was then determined. At a noted time a measured amount of ferric chloride solution was added, the whole vigorously shaken, the "plunge" electrodes replaced, and the change in conductivity then followed at known intervals of time.

In the following Tables, XX, XXI, XXII and XXIII, are given the results obtained. Under "equivalent conductivity" is given the conductivity of the ferric chloride in the mixed solution after correcting for

the conductivity of the added colloidal ferric hydrate in the solution. This had an appreciable conductivity, as already stated, due to the presence of some crystalloids still remaining in it. In Table XXIII, however, the values given are the uncorrected conductivity values for the mixture—the specific conductivity of the colloidal solution not having been in this case accurately determined. A comparison of the initial corrected values in Tables XX, XXI and XXII, namely, 172.6, 171.2 and 172.6, with the initial value found for the pure ferric chloride solution 172.8 (Table VI), shows that they agree almost exactly whence it is safe to conclude that the conductivity of the mixture may be assumed additive. We have therefore, for convenience of comparison in plotting, corrected all the values given in Table XXIII by — 8, thus reducing the initial values of the conductivity of the ferric chloride to that found in the other solutions.

TABLE XX.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.000116$. $t = 25°.0$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 20	172.6	13 40	174.9
2 20	172.8	34 20	177.8
3 50	173.3	36 0	178.1
5 15	173.6	46 10	179.5
6 45	173.9	54 0	180.8
8 20	174.1	1 5 0	181.7
9 30	174.2		

TABLE XXI.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.000232$. $t = 24°.96$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
1 35	171.2	54 50	186.1
3 5	172.4	1 15 0	192.6
4 30	172.7	1 36 0	199.0
6 35	173.2	1 40 0	200.0
7 40	173.6	3 31 0	222.2
10 50	174.3	3 36	223.2
25 20	177.8	23 51	262.6

TABLE XXII.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.00116$. $t = 24°.96$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
2 30	172.6	29 50	200.7
4 45	176.0	40 30	207.3
5 30	176.9	46 30	211.9
13 0	184.8	.....	.....
20 30	192.5	19 5	277.1

TABLE XXIII.

$FeCl_3$ $C = 0.00750$. $Fe(OH)_3$ $C = 0.00580$. $t = 25°.0$.

Time elapsed. h. m. s.	Equivalent conductivity.	Time elapsed. h. m. s.	Equivalent conductivity.
50	180.4	11 15	222.0
1 15	187.0	13 45	225.8
2 15	197.0	16 40	229.7
2 35	198.6	19 20	232.5
3 5	200.7	22 10	235.8
3 35	203.0	31 0	244.0
4 5	204.8	1 2 20	257.5
4 30	206.3	1 41 0	267.4
5 15	208.3	4 15 0	284.6
6 15	211.2	.....	.....
7 35	214.7	21 32	312.1

The effect of the presence of increasing amounts of colloidal hydrate on the course of the reaction is most readily seen from plot 5, made from the date in the preceding tables.

It is seen at once from this plot that, as anticipated, the presence of colloidal hydrate accelerates the reaction to a very marked extent. In all cases the reaction starts immediately upon diluting the chloride, the initial lag of 20 minutes observed in the neutral solution being thus completely absent. Moreover, the increase in the initial rate of the reaction is approximately proportional to the concentration of the added colloidal hydrate. This in the four solutions investigated is present in the ratio, 1 : 2 : 10 : 50, while the increase of conductivity per minute is approximately in the ratio 0.2 : 0.4 : 1.4 : 10, or 1 : 2 : 7 : 50. The first three values are the rates during the first five or six minutes of the reaction; the last,

during a still shorter interval of two and a half minutes, as this last reaction slows up very quickly after the first few minutes. It seems

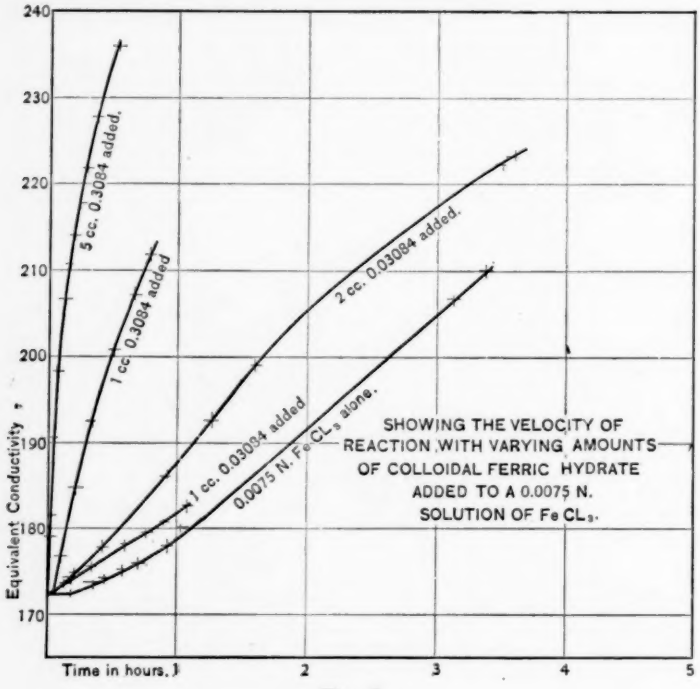

Fig. 5.

probable, therefore, that other things being equal, the presence of colloidal hydrate exerts a catalytic action nearly proportional to its concentration.

III.

The Effect of a Magnetic Field on the Rate of the Reaction.

It has now been pretty well established[1] that chemical reactions may in certain cases be modified when they are caused to take place in a powerful magnetic field. Wiedemann[2] has further shown that the magnetic moment of a ferric chloride solution is

[1] Wiedemann's Lehre von der Electricität for the early literature, vol. 3, p. 1129; Liesesang, Beibl. 15, 123; Braham, Beibl. 16, 304; Andrews, Proc. Roy. Soc. 52, 114, 1892; Nichols, Am. J. of Sc. 31, 372.

[2] Lehre von der Elect., vol. 3, p. 964.

much diminished by the formation of colloidal ferric hydrate. It was therefore thought to be not without interest to investigate whether or not the velocity of the colloidal formation studied above, was in any way affected by a magnetic field. As our experiments gave only negative results, the numerous preliminary experiments and arrangements of apparatus will be passed over and only the final arrangement briefly described.

It was desired to compare the rate of the colloidal formation in two exactly similar solutions at exactly the same temperature, the one placed in a strong magnetic field, the other removed from it. Any ordinary form of thermostat was of course out of the question, on account of the small distance between the poles of the electro-magnet between which it was desired to place the cell. We arranged, therefore, as thermostats, two duplicate Beckmann boiling-point tubes, provided with condensers and containing pure ether, boiling at 33° C., and used test-tubes fitted into these ether jackets and provided with plunge electrodes as conductivity cells.

TABLE XXIV.

$C = 0.0040$ *approximately.*

h. m. s.	$k \times 10^{-4}$ I.	$k \cdot 10^{-4}$ II.	h. m. s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.
3 59 30	Diluted.		4 20 30		8.01
4 4 45		6.95	21 10	8.04	
5 30	7.12		23 30		8.10
6 50		7.22	24 0	8.12	
7 15	7.29		26 35		8.16
7 50		7.30	29 0	8.26	
8 50	7.38		32 5		8.29
9 25		7.50	32 50	8.33	
10 5	7.53		39 20		8.43
10 50		7.60	40 15	8.44	
12 0	7.66		47 50		8.53
13 0		7.69	48 30	8.54	
14 20	7.78		5 6 5		8.70
14 50		7.79	8 0	8.71	
16 15	7.87		11 20		8.72
17 0		7.88	13 20	8.75	
17 35	7.93		14 30		8.75
18 55		7.96			
19 40	7.99				

TABLE XXV.

$C = 0.0040$ *approximately.*

h. m. s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.	h. m. s.	$k \times 10^{-4}$ I.	$k \times 10^{-4}$ II.
1 37 0	Diluted.		2 3 50	8.14	
1 40 45	6.50		4 20		8.12
41 50		6.63	6 20	8.19	
42 25	6.78		7 0		8.20[1]
42 55		6.81	10 15	8.29	
43 25	6.91		10 55		8.30[1]
44 0		6.94	16 55	8.43	
44 40	7.04		17 35		8.43[1]
46 35		7.22	24 0	8.54	
47 15	7.29		24 35		8.55[1]
47 45		7.32[1]	27 35	8.59	
48 55	7.42		28 5		8.60[1]
49 30		7.46[1]	41 50	8.75	
50 55	7.56		42 25		8.76[1]
52 20		7.61[1]	45 55	8.79	
54 40	7.79		46 15		8.80[1]
55 10		7.79	3 6 25	8.93	
58 30	7.95		3 7 0		8.94[1]
2 0 0		7.99			

One of these was set up between the poles of a powerful electromagnet, and the other at some distance away. Direct experiment then showed that the temperatures of aqueous solutions placed in the cells could be kept the same to 0.01° for several hours. The procedure was to allow the ether to boil for some minutes in both thermostats in order to bring the dry cell and electrodes placed therein to the proper temperature ; to then dilute the ferric chloride to the desired strength in a separate flask containing water previously weighed and heated to the boiling point of ether ; and then to quickly transfer the solution thus prepared to the two measuring cells.

The current in the electromagnet could be regulated and thrown on or off at will. The strength of the field in which the solution was placed was determined by the change of resistance of a bismuth coil of wire placed in the field. The strength of field was thus found to be about 1850 lines per sq. cm. Table XXIV contains the results

[1] Signifies that II was in the magnetic field.

of a blank run, both cells being unmagnetized. The values given are specific conductivities at the temperature of boiling ether (33°). They are shown in plot 6, where it is seen that the two curves prac-

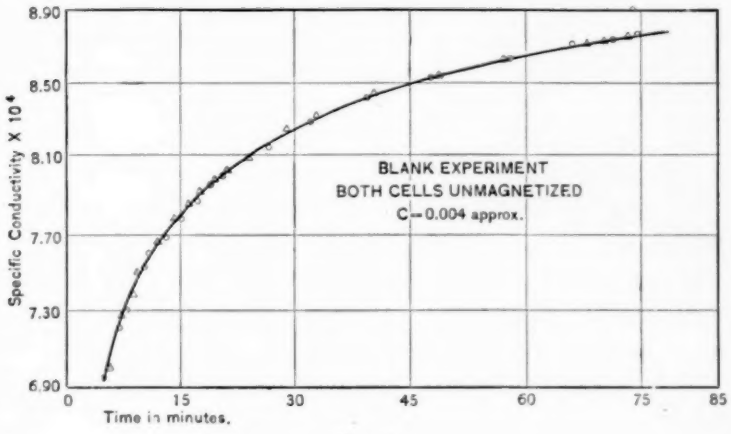

Fig. 6.

tically coincide throughout, thus confirming the accuracy of the cell constants and the constancy of temperature of the ether jackets.

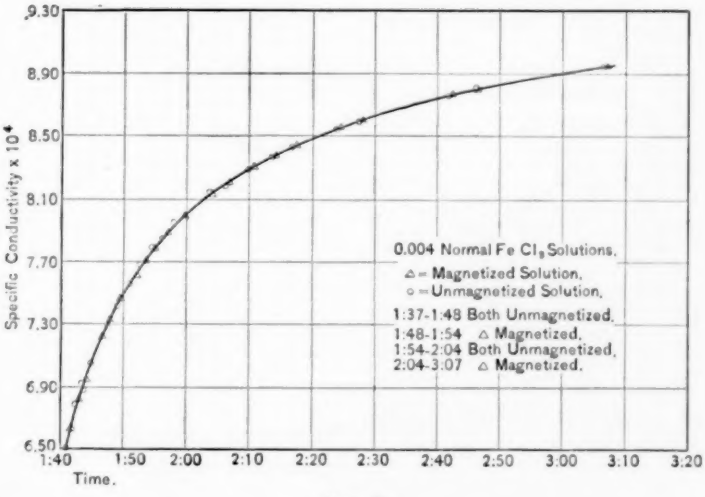

Fig. 7.

Table XXV contains the results of a run in which one cell remained unmagnetized, the other alternately magnetized and unmagnetized.

The results of both series are shown in plot 7. The curves coincide throughout, showing that no change in the rate of reaction was produced by the magnetic field. Numerous other runs confirmed this result, so that the conclusion may be drawn that the rate of formation of colloidal hydrate in ferric chloride solutions is not affected by the presence of a magnetic field of strength not greater than about 2000 lines per sq. cm.

CONCLUSION.

The principal results of this investigation may be summed up as follows:

1. The effect of lowering the temperature is to very greatly diminish the rate of formation of colloidal ferric hydrate, and to increase the initial lag in the reaction.

2. The hypothesis previously advanced to account for the acceleration of the reaction when once started is confirmed. The presence of colloidal hydrate exerts a very marked catalytic action causing the reaction to be accelerated by an amount approximately proportional to the amount of colloidal hydrate present in the solution.

3. No effect of a magnetic field could be detected on the course of the reaction.

ROGERS LABORATORY OF PHYSICS,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, June, 1900.

PRELIMINARY NOTE ON THE EFFICIENCY OF THE ACETYLENE FLAME.[1]

By Edward L. Nichols.

IN the study of flames or of glowing bodies of any kind, considered as devices for the production of light, and it is upon such devices that artificial lighting depends, the question of efficiency is of great importance. The complete solution of the problem involves the determination of the ratio of the light-giving radiation to the total energy expended in producing it; and the measurement of this quantity, *the total efficiency*, usually involves as an intermediate step, the determination of *the radiant efficiency*, which is the ratio of the luminous or light-giving radiation to the total radiation.

In the measurement of radiant efficiencies at least four distinct methods have been employed.

Julius Thomsen,[2] who was a pioneer in this field of research, read a paper at Stockholm in 1863, entitled *The Mechanical Equivalent of Light*, in which he applied the method of Melloni to the separation of the light-giving from the non-luminous radiation. Thomsen used a water cell containing a layer of liquid 20 cm. in thickness, by the interposition of which between the source of light and the thermopile used in measuring its radiation, he sought to cut off the dark heat. He studied the flames of spermaceti candles, of ordinary illuminating gas, and of the moderator lamp; determined the energy, expressed in calories per minute, emanating by radiation from these sources, and compared it with the calories of luminous energy. Blattner[3] in 1886 applied the second method under consideration, that of immersing the source of light in a calorimeter of glass to incandescent lamps under varying supplies of current. Merritt and Ryder[4] in the same year applied both methods to incan-

[1] A paper read before the American Physical Society, June 27, 1900.

[2] Thomsen, Poggendorff's Annalen, 125, p. 348.

[3] Blattner, Das optische Nutzeffect der Glühlampen, Fraunfeld, 1886.

[4] Merritt, American Journal of Science, vol. 37, p. 67.

descent lamps. They used a solution of alum instead of water, and made the very necessary correction for the infra-red radiation which passes through the cell by the interposition of a second cell containing a solution of an opaque solution of iodine in carbon disulphide. They checked the results obtained by this method by submerging the lamp in a calorimeter through which a constant flow of water was maintained, and measuring the temperature of the water upon entering and leaving the vessel. The non-luminous radiation was in great part retained by the water surrounding the lamp, while the light-giving rays were largely transmitted by the liquid and by the glass walls of the calorimeter. The necessary corrections were determined by a study of the transmitting power of the glass and water for dark rays, and their absorbing power for light. The total radiation was computed by measurements of the electro-motive force at the terminals of the lamp and the current traversing the filament. This quantity was likewise checked by placing the lamp in a calorimeter with opaque walls and measuring the heat energy delivered to the water directly.

Staub[1] in 1890 studied the radiant efficiency of the illumination from vacuum tubes when excited by means of the electrical discharge; for which purpose he employed a modified form of the Bunsen ice calorimeter.

Determinations of radiant efficiency have likewise been carried out by the method of the thermopile and water-cell by Nakano[2] and by Marks[3] in the case of the arc lamp, by Rogers[4] in his study of magnesium as a source of light, by Miss Crehore[5] (Mrs. F. Bedell) who investigated in this manner the efficiency of the lime light, and by others.

A fourth and far more rigorous method (that of obtaining the distribution of energy throughout the visible and invisible spectrum

[1] Staub, Inaugural Dissertation, Zürich, 1890; also Beiblätter zu den Annalen der Physik, 14, p. 538.

[2] Nakano, Transactions of the American Institute of Electrical Engineers, vol. 6, p. 308 (1889).

[3] Marks, Transactions of the American Institute of Electrical Engineers, vol. 7, p. 175 (1890).

[4] Rogers, American Journal of Science, vol. 43, p. 301 (1892).

[5] Nichols and Crehore, PHYSICAL REVIEW, vol. 2, p. 161 (1894).

and comparing the areas) of determining the radiant efficiency is due to Langley[1] and has been applied by him to sunlight, to various artificial illuminants, and to the light from the Cuban fire fly. The difficulties in the way of carrying out this method properly are, however, extremely great and it is frequently a question whether under the ordinary degree of command over the conditions of the experiment, the method yields a better result than the more convenient procedure invented by Melloni and developed by Tyndall and by the various subsequent workers just cited.

Upon the problem of the total efficiency of sources of light, much less has been done than upon the radiant efficiency. Thomsen in the article already cited, estimated that in the case of the candle and of the moderator lamp the total development of heat was about three hundred and fifty times as great as the luminous energy of the flame, and that in the case of gas flames it was approximately one thousand times as great. Rogers determined the heat of combustion of magnesium, and, by means of a modification of Thomsen's method, ascertained the relation of the luminous radiation from a mass of the burning metal to the total heat produced by the reaction. Various other writers,[2] in the course of discussions upon the relative merits of electric lighting and of artificial illumination by means of flames, have attempted to express in one way or another the efficiency of the various methods, but actual measurements by direct experiment have been very few.

Experiments are in progress under the direction of the writer, by means of which the efficiency of the acetylene flame is to be directly determined with as high a degree of accuracy as the nature of the case may permit. For this purpose, the radiant efficiency is to be computed in two ways. First, by the method of Melloni, and second by the exploration of the spectrum and the comparison of the areas enclosed by the curve within and without the limits of visibility. The heat of combustion of acetylene gas, carefully prepared and thoroughly purified, is to be determined, and the total radiation

[1] Langley (see the well-known report of the Mt. Whitney expedition, and subsequent memoirs).

[2] See in particular, Preece; Nature, vol. 38, p. 496, (also B A. Report (1888), or the table computed from data by Preece and published by the present writer in the Transactions of the American Institute of Electrical Engineers, vol. 6, p. 175 (1889).

from a flame of this gas found by a modification of Thomsen's method. Measurements of the amount of gas supplied to the flame will then make it possible to ascertain with considerable accuracy the total efficiency of this source of light.

Preliminary measurements from which it is possible to compute the value of the efficiency of acetylene flames obtained from the ordinary gas, such as is produced from the usual form of generators in which calcium carbide is thrown into water, are already completed and since the interest in this source of illumination is at present widespread, it seemed worth while to report these preliminary results without waiting for the completion of the more refined experiments which are to follow.

RADIANT EFFICIENCY.

These preliminary experiments naturally divide themselves into three parts, of which those upon the radiant efficiency were carried out by Messrs. Stewart and Hoxie. Their apparatus differed in several respects from that used by most of the earlier observers. Instead of a thermopile, they employed a bolometer of iron wire. The acetylene flame was of the flat type produced by the well known *Naphey* burner. Between the flame and the bolometer, a water cell was moved in and out. This cell was much smaller than those commonly employed, the dimensions being such that the rays traverse 1 cm. of water and 0.4 cm. of glass. The use of water instead of solutions of alum frequently employed in such work is justified by the investigations of Ernest Nichols[2] upon the perviousness of these and other substances to the infra-red rays of the spectrum. It will be seen by reference to Fig. 10 in that article, that water, potassium alum, and ammonium alum, all possess approximately the same transmitting power between the red end of the spectrum and wave lengths 1.5 μ where they all become opaque.

From thirty-nine sets of readings Stewart and Hoxie obtained the value 0.207 for the ratio of the light transmitted through this cell to the total energy reaching the thermopile when it was interposed. That this ratio does not express the true relation between the light-giving and the total energy from the flame is obvious.

[1] Nichols, PHYSICAL REVIEW, vol. 1, p. 1, 1893.

Water and glass, on the one hand, absorb a certain proportion of the light and there are four reflecting surfaces at which losses occur. On the other hand, water transmits a considerable amount of non-luminous energy. The degree of this perviousness to rays lying beyond the limits of the visible spectrum is known to be considerable [1] and it is clear that, contrary to the view expressed by Thomsen in his article on the *Mechanical Equivalent of Light*, a large correction must be applied. This correction was determined in the usual way. Iodine was dissolved in carbon disulphide, the solution being of such strength as to be opaque to visible rays. The water cell and the cell containing the iodine were set up in such positions that the rays from the acetylene flame passed through both in the order named, on their way to the bolometer. The iodine cell was of the same size as that which contained the water. It was moved in and out, and twenty-two sets of readings were taken from which it appeared that the iodine cell absorbed fifty-one per cent. of the energy which passed through the water cell. Upon the assumption that the iodine cell is entirely transparent to the rays of the infra-red spectrum and entirely opaque to visible rays, we obtain for the radiant efficiency of the acetylene flame

$$0.51 \times 0.207 = 0.105.$$

This value can only be considered as approximate since no corrections were made for reflection from the surfaces of the glass, nor for the absorption of light by water, nor of infra-red energy by the iodine. From the following statement of the theory of these corrections, worked out by the observers, it will be seen that the losses in the water and iodine cells tend to annul each other and that consequently they may be ignored altogether without serious error.

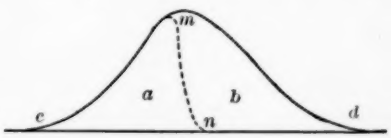

Fig. 1.

Let the curve *cd* in Fig. 1 represent the distribution of energy in the spectrum of the flame, let the line *mn* mark the limit of the spectrum transmitted by water, and let the total energy of the spectrum from the flame be A; then

[1] See Ernest Nichols, l. c.

$$a + b = A \tag{1}$$

By moving the water cell in and out of the path of the rays, we are able to determine the ratio

$$\alpha = \frac{a'}{A}$$

where a' is the value of a, less losses due to reflection and to absorption by water. Let the area d (Fig. 2) be that portion of the energy transmitted by the iodine solution and let e be that which will traverse both solutions. If the water cell be kept in the path of the rays and the iodine cell be moved in and out, we are able to obtain from observation the ratio

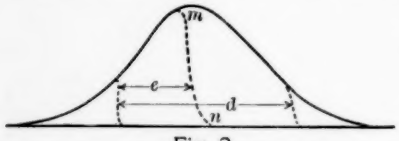

Fig. 2.

$$\varepsilon = \frac{e'}{a'}$$

in which e' is e, minus the losses by reflection and by absorption in the water and in the iodine. If c be the visible energy of the spectrum and c' the part of the same transmitted by water; then, since for a given surface and solution, the loss by reflection and by absorption is proportional to the intensity, we have

$$e' = (a' - c')\,(1 - k_i) \tag{2}$$

where k_i is the coefficient for the reflection and absorption by the iodine cell in the infra-red. We may write in like manner

$$c' = c(1 - k_w) \tag{3}$$

where k_w is the coefficient for the water cell in the visible part of the spectrum. From these, by substitution, we have

$$e' = a' - c - (a' - c')k_i + ck_w \tag{4}$$

and substituting this value of e', we have an expression for the energy absorbed by the use of water and iodine cells

$$\varepsilon = \frac{a' - c - (a' - c')k_i + ck_w}{a'}. \tag{5}$$

Now the approximate radiant efficiency 0.105, given as the result of these preliminary experiments is

$$E_{(\text{approx.})} = \left(1 - \frac{c'}{a'}\right)\frac{a'}{A} = \frac{c + (a' - c')k_i - ck_w}{A}, \qquad (6)$$

while the true radiant efficiency is

$$E = \frac{c}{A}.$$

In equation 6, $(a' - c')k_i$ is the loss due to reflection and to absorption of the infra-red rays in the iodine cell, while ck_w is the loss due to reflection and to absorption of the light rays by water. If these

TABLE I.

Radiant efficiency of various sources of light.

Source.	Observer.	Luminous radiation. Total radiation.
Sperm candle.	Thomsen.	0.0210
Paraffine candle.	Rogers.	0.0153
Moderator lamp.	Thomsen.	0.026
Illuminating gas.	Thomsen.	0.0197
" "	Langley.	0.0240
" (bat's wing).	Rogers.	0.0128
" (argand).	Rogers.	0.0161
Incandescent lamp.	Blattner.	0.05 to 0.06
" "	Merritt.	Various values up to 0.06
" "	(From integration of Abney and Festings' curves).	0.055
Welsbach mantle.	Stebbins.	0.02 to 0.07
Lime light (new).	Crehore.	0.14
" (old).	"	0.084
ACETYLENE.	Stewart and Hoxie.	**0.105**
Arc light (Foucault).	Tyndall.	0.104
"	Nakano.	0.104
"	Marks.	0.08 to 0.13
Magnesium light.	Rogers.	0.125
Geissler tubes.	Staub.	0.32

two losses are equivalent, the method gives us the true radiant efficiency c/A without attempting any further corrections. In precisely similar cells, the losses by reflection will be nearly equivalent. Data for the absorption losses in water are available but the curves

for solutions of iodine have, so far as I know, never been obtained. Since the two quantities tend to annul each other, there is probably less error involved in neglecting corrections altogether than in correcting for the water cell and in attempting without requisite data to correct for the losses in the iodine. While the nature of these losses is not accurately known, it is probable that the uncorrected result is at least approximately true.

These preliminary measurements give to the acetylene flame a position in the scale of radiant efficiencies very nearly equal to that of the arc light. The relation which different sources of light bear to each other in this respect may be seen from the table on page 221, which contains a list of previous determinations of radiant efficiencies.

HEAT OF COMBUSTION.

The preliminary experiments upon the heat of combustion of acetylene, necessary to the computation of the efficiency of the flame, were undertaken at the writer's suggestion by Mr. H. A. Rands. The gas used was the ordinary unpurified acetylene obtained from a generator in which the carbide of calcium was dropped into a large mass of water. The gas produced by this so-called wet process contains a larger percentage of acetylene and is less subject to polymerism than where water is applied in small quantities to the carbide. Unless special processes of purification are employed, however, the product is by no means pure acetylene. Analyses of several samples of the gas generated from the same lot of carbide as that used in these experiments showed from 20% to 25% of other gases, chiefly inert. The Favre and Silbermann calorimeter was used, the combustion jet being slightly modified so as to secure complete and smokelesss burning of the acetylene. Various samples of the gas taken on different days, gave a mean result of approximately 10,000 calories for the heat of combustion. This is considerably below the theoretical value of 12,200 as given by Pellissier, but the difference is essentially what one would expect from the analysis of the gas itself. In the completion of the investigation, it is proposed to make an extended series of determinations of the heat of combustion of acetylene after the gas has been

subject to thorough purification, and to give the analyses of the gas employed.

Ratio of Total Heat Generated to Total Radiation.

Upon the relation between the total heat generated in the flame and the heat dissipated in the form of radiation, our experiments are still in progress. This portion of the subject is being studied by Mr. Albert Ball. His method, the results of the preliminary application of which only are given in the present note, is as follows:

A thermopile is connected in closed circuit with a galvanometer of suitable sensitiveness. At a convenient distance from the face of the thermopile, the acetylene flame is mounted, and between the two is a shutter by means of which the aperture in an intervening screen can be opened and closed by an observer situated at the telescope of the instrument. Readings are made by removing the shutter from the aperture for an interval of time corresponding to that of the first swing of the galvanometer. As soon as the needle makes its first turning point, the aperture is closed so that further heating of the face of the thermopile may be avoided. It is well established that the deflection, counting from the original position of the needle to its first turning point, is, under these conditions, always proportional to the total deflection which the galvanometer would take.[1] The method is one which enables a great saving of time and also reduces the risk of error from the shifting of the zero point. To calibrate a thermopile and galvanometer thus used, the following modification of Thomsen's procedure was employed. A spherical flask with its outer surface blackened was filled with water and its center was placed exactly in the position occupied by the flame in the operation just described. In the bottom of the flask, a coil of German silver wire was mounted, the terminals of which were brought out through the neck by means of copper lead wires of low resistance. By means of this coil, the water in the flask was heated to a temperature sufficient to produce upon the galvanometer an effect comparable to the radiation from the flame, and to maintain it at that temperature permanently. The shape and position of this coil was found to be a matter of considerable importance, and it was

[1] See Merritt, American Journal of Science, vol. 41, p. 417.

only after several trials that a form of coil was obtained which gave a satisfactorily even distribution of temperature throughout the flask. By giving this coil the form of a spiral wound upon a cylinder with axis horizontal and placing the same as near the bottom of the flask as possible, and centering it carefully, it was found that the convection currents were of such a character as to maintain the water in the flask at a constant temperature throughout. Exploration of the temperature in different portions showed variations amounting only to a small fraction of a degree.

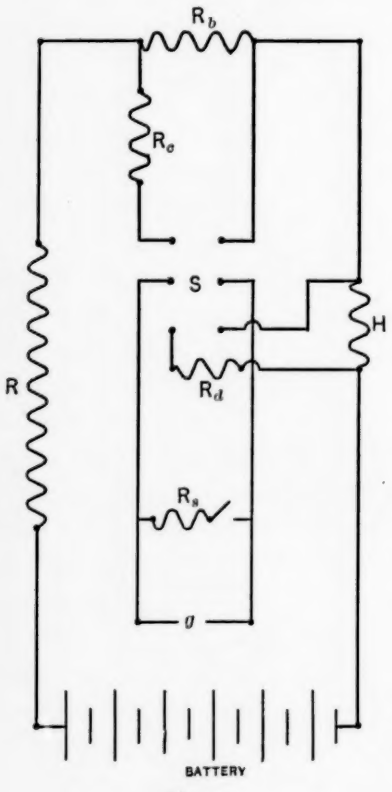

Fig. 3.

The electrical connections, by means of which the current from the coil was adjusted and measured, and the fall of potential between its terminals was determined are shown in Fig. 3.

The source of the current was a storage battery in circuit with which in series were an adjustable resistance (R), the heating coil (H), and a standard coil (R_b) of manganin wire, having a value of .1 ohm. The current was measured by placing a sensitive d'Arsonval galvanometer (g) in multiple with this standard coil and measuring the fall of potential through the same. The galvanometer was calibrated by means of a Clark cell. Wires connected with the terminals of the heating coil were carried to the same galvanometer, a six point switch (S) being so arranged that the instrument could be used alternately for measuring the fall of potential in the heating coil and in the standard coil (R_b) already described. Suitable resistances, (R_c) and (R_d), were placed in the galvanometer circuit and the instrument itself was shunted around a resistance

R_s by means of which its deflection could be reduced to the proper size. The delicacy of this galvanometer was such that in order to secure the desired reading, R_d was given a value of 1,000,000 ohms, and R_c 9,930 ohms, which latter, together with the resistance of the galvanometer itself, made the total resistance of that circuit 10,000 ohms.

The energy imparted to the flask was computed from the electrical measurements and to determine what proportion of this energy was lost by radiation and what by convection, the flask was placed in a bell-jar from which the air was subsequently removed. The loss by conduction was, for the purpose of these preliminary determinations, assumed to be negligible.

Assuming the loss of heat by radiation to be the same for a given temperature at the surface of the flask in air and in vacuo, and that all the heat developed in the flask by the action of the electric current is, in vacuo, dissipated by radiation, we may plot a curve having as abscissæ the units of heat radiated at different temperatures as computed by means of these electrical measurements when the flask is in vacuo, and the deflection produced when the thermopile is exposed to the flask *in the air* at the same temperatures. This curve serves to enable us to find *directly* the total amount of radiation from *any source* radiating equally in all directions, which may be placed in the position of the center of the flask, by means of the deflection of the galvanometer exposed to it under conditions similar to those made with the flask in situ. It is true that there is a small error due to the fact that the flask is not a perfect sphere and that the radiation from it is not strictly the same in all directions. It is likewise true that the distribution of radiation from the acetylene flame is not perfectly uniform, but these errors are so small that it was not necessary to consider them, in this preliminary determination of the efficiency.[1] It is obvious that the ratio of total radiation to total energy of combustion must be a function of the gas pressure and that it will reach a maximum for some particular size of the flame. With increasing pressures, the tendency is for the gases to be hurried away from the hot center of the flame so that there will be

[1] For a curve of horizontal distribution of intensities, see a paper on the acetylene flame read by the present writer before The Franklin Institute in March, 1900.

increasing losses of heat by convection with increasing pressure. Up to a certain point, this loss is overbalanced by the improved conditions under which combustion takes place, and there will be a value for the pressure at which, for any given burner, the efficiency will be greatest. Mr. Ball's work in these preliminary experiments divided itself, as will appear from the foregoing, into two parts. First, a calibration of the flask for convection losses, and secondly, the reading of the galvanometer when the thermopile was exposed to the action of the flame. The range of temperatures of the flask lay, as will be seen by inspection of the following table, between 81.8° and 96.1°C.

TABLE II.

Relation between temperatures of flask, galvanometer throws, and the total radiation of heat.

Temperatures of flask.	Total heat radiated (in calories per second).	Throw of the galvanometer.	Temperatures of flask.	Total heat radiated in calories per second).	Throw of galvanometer.
81.8°C.	6.976	10.05 s. d.	90.1°C.	7.619	12.35 s. d.
84.8	7.143	11.15	92.6	7.917	12.70
86.1	7.238	11.35	94.2	8.143	13.10
88.0	7.393	11.78	96.1	8.452	13.70

The total heat radiated from the flask at these temperatures is computed from the electrical measurements already described. The throw of the galvanometer when exposed to the flask at the same temperature in air is given in column 3. From these, a curve of the sort already alluded to for the radiation between heat radiation per second and galvanometer throws was drawn (Fig. 4).

To use the method just described, for the determination of the ratio of radiated to total heat, the acetylene flame was substituted for the heated flask, the deflection produced when the thermopile was exposed to its action being interpreted by means of the curve given in Fig. 4. Gas for the supply of this flame, passed first into an automatic regulator, the construction of which has been given in a previous paper.[1] From this regulator, it passed through an experimental gas meter reading in liters per minute, thence to a

[1] Nichols, l. c.

tube provided with a side arm leading to an open tube manometer, and thence to the flame. The flame was set up, as the flask had been in the calibration experiments, in an inner room quite free from drafts, through the wall of which an aperture was cut, with a

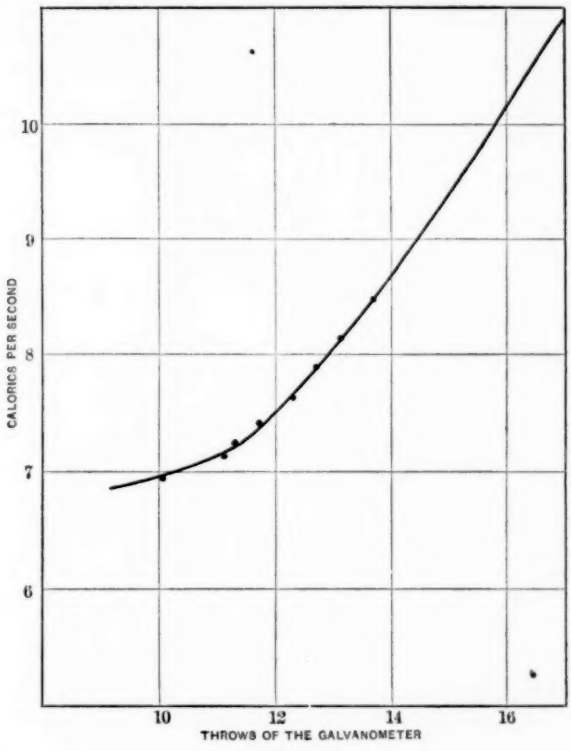

Fig. 4.

double shutter capable of being raised and lowered. Opposite this opening the thermopile was mounted in such a position that one of its faces would receive the radiation from the flame. This thermopile, as has already been indicated, was held in closed circuit with the galvanometer and the reading was made by alternately raising and lowering the shutter. In computing the results of these measurements, the heat of combustion found by Mr. Rands in the experiments already described (namely, about 10,000) was assumed to be correct. Two determinations were made, the data for which together with the results obtained are given below.

Experiment A.

Molecular weight of acetylene (C_2H_2), 26.

Molecular volume of acetylene (760 mm. and 273° abs.), 22.4.

Pressure at which the gas was supplied to the burner, 766 mm.

Temperature of the gas, 293° (abs.).

Volume of 26 grams of the gas at above pressure and temperature, 23.85 liters.

Rate of delivery of gas, 0.174 liters per minute, or 0.00316 grams per second.

Total heat produced by the reaction per second, $0.00316 \times 10{,}000 = 31.6$.

Deflection of galvanometer, 11.0 s. d.

Calories indicated by flame per second, as indicated by above deflection, 7.13.

$$\text{Ratio: } \frac{\text{total radiation}}{\text{total heat}} = \frac{7.13}{31.6} = 0.225.$$

TOTAL EFFICIENCY; assuming the radiant efficiency to be 10.5%; $0.225 \times 0.105 = 0.0236$.

In experiment *A* the flame was below normal size.

Experiment B.

Rate of delivery of gas, 0.297 liters per minute, or 0.00539 grams per second.

Total heat produced by the reaction, per second, $0.00539 \times 10{,}000 = 53.9$.

Deflection of the galvanometer, 16.12 s. d.

Calories radiated by flame per second, as indicated by above deflection, 10:25.[1]

$$\text{Ratio: } \frac{\text{total radiation}}{\text{total heat}} = \frac{10.25}{53.9} = 0.190.$$

TOTAL EFFICIENCY, assuming the radiant efficiency to be 10.5%, $0.190 \times 0.105 = .0199$.

[1] This value is much less reliable than that used in experiment *A* because it is taken from a portion of the curve not covered by the calibration observations. It is unlikely, however, that the extrapolation is sufficiently at fault to vitiate the conclusion that the efficiency of this flame, which was of fully normal size, was lower than that of the foregoing.

These values are many times greater than the corresponding values for ordinary gas and oil flames. They are at least double the corresponding value for the arc light under the most favorable conditions for the latter source.

The magnesium flame alone, which, according to Rogers, has a total efficiency of 0.1025, is, on account of the very small loss by convection and the very high radiant efficiency, superior to acetylene in this respect.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
June 20, 1900.

THE DEVELOPMENT OF KATHODE RAYS BY ULTRAVIOLET LIGHT.[1]

BY ERNEST MERRITT AND OSCAR M. STEWART.

IT has long been known that the discharge of negative electricity under the influence of ultraviolet light is the result of convection. All observers agree in the conclusion that negatively electrified particles of some sort act as the carriers of the escaping charge; whether these particles come from the surrounding air, or from the layer of condensed gas upon the electrified surface, or from the material of the charged body itself, is not yet definitely known.

In air at ordinary pressures the motion of the particles is relatively slow, even for a large potential gradient. But as the pressure is reduced the speed rapidly increases, being approximately proportional to the reciprocal of the pressure. The experiments[2] upon which this law is based extend only to a pressure of 34 mm.; but that the increase in speed continues with further exhaustion is indirectly shown by the earlier experiments of Righi[3], who found that at low pressures the paths followed by the electrified particles no longer coincided with the electrostatic lines of force, as is the case at ordinary pressures, but became straighter and more nearly coincident with the normal to the charged surface.

[1] A brief account of the experiments here described was published in the Physikalische Zeitschrift, May 5, 1900. Since that time an article by Lenard, dealing with the same subject, has appeared in the Annalen der Physik (Vol. 2, p. 359, 1900), being republished from the Wiener Berichte (Vol. 108, Abth. IIa, p. 1649, 1899). The experiments of Lenard upon the magnetic deflectability of the photo-electric rays are similar to those here described, and, like the latter, give a *direct* proof that the rays are deflected. Some differences in method will, however, be noticed, and we have therefore left the present article unaltered. Except in the case of the magnetic deflectability of the rays the work of Lenard deals with a different phase of the subject from that here considered. We regret that the delay in the appearance of the Wiener Berichte prevented us from referring to Lenard's article in our original communication.

[2] Rutherford, Camb., Phil. Soc. 9, p. 401, Feb. '98.

[3] Acc. de Lincei 6, p. 81; Acc. di Bologna 10, p. 85; Wiedemann's Beiblätter 14, p. 1167.

This peculiarity of the photo-electric discharge at low pressures brings to mind the similar behavior of the negatively charged corpuscles which form the kathode rays. In each case we have to deal with a stream of negatively charged particles repelled from the kathode surface, and moving so rapidly, and with so little frictional resistance, that the path followed is only slightly influenced by the form of the electric field. In recognition of the analogy between the two phenemona, and for the sake of brevity, we shall refer to the stream of charged particles in the case of the photo-electric discharge as photo-electric kathode rays, or *photo-electric rays.*

The photo-electric discharge, while unaffected by magnetic influences at ordinary pressures, may be greatly diminished, or even suppressed, by a magnetic field when the discharge occurs in vacuo. In order to produce this effect the field must have a component parallel to the charged surface, and therefore at right angles to the path of the charged particles. It has been suggested by Elster and Geitel[1] that the effect is due to a deflection of the charged particles or ions in passing through the magnetic field. If this view is correct the phenomenon must be regarded as closely analogous to the well known magnetic deflection of the kathode rays.

Considered in connection with certain speculations regarding the mechanism of the discharge produced by illumination, the facts just mentioned have led us to believe that at low pressures the photo-electric discharge is accompanied by the development of true kathode rays: in other words, that the photo-electric rays are identical in character with the kathode rays produced in an ordinary vacuum tube. Since the experiments to be described in this paper were begun, this view has received strong support from the work of J. J. Thomson.[2] Using a form of apparatus capable of quantitative work, Thomson has not only found very convincing indirect evidence of a magnetic deflection of the photo-electric rays, but has also been able to determine the ratio of the charge carried by each particle to its mass. The values obtained for this ratio range from 5.8×10^6 to 8.5×10^6. In the case of the corpuscles which constitute the kathode rays the values found for the corresponding

[1] Wied. Ann. 41, p. 166, 1890; Wien. Ber. 97, Abth. IIa, p. 1175.
[2] Phil. Mag. 48, p. 547.

ratio lie between 6.3×10^6 and 18.65×10^6. When we recall the experimental difficulties of such determinations the agreement is to be regarded as a good one, and it seems highly probable, as suggested by Thomson, that the carriers of the negative charge are the same in both classes of phenomena.

The experiments described in the present communication were undertaken in order to test the conclusion that kathode rays may be developed, at low pressures, by the action of ultraviolet light. Taking up in turn the well known properties of the ordinary kathode rays, we have tried to show experimentally that similar properties are possessed by the photo-electric rays. In the majority of cases the attempt has proven successful. Thus we have been able to show that the rays are magnetically deflected; that they ionize the gas through which they pass; and that their motion is modified by electrostatic forces. We have not been able to observe fluorescence produced by the photo-electric rays; nor do they appear to develop Röntgen rays. The apparent absence of these two phenomena is sufficiently explained by the feeble intensity of the rays used by us, and by the crude character of the experiments made to detect them.[1]

APPARATUS.

The general plan of the vacuum tube used is shown in Figure 1. The tube was mounted vertically with the kathode K at the bottom and the electrodes L, M, and R at the top. The kathode was a short zinc cylinder with its upper end carefully polished. Being mounted in a glass stopper it could be readily removed for polishing. K was connected to the negative terminal of a dry pile and thus kept permanently charged. Immediately above the kathode K was the anode A, which consisted of a ring of rather large aluminium wire. The ring is shown only in projection in the figure, the plane of the ring being perpendicular to the plane of the figure. The three

[1] Since the kathode potential in our experiments was only about 1000 volts, we had little hope of detecting any Röntgen rays. Only one exposure, lasting an hour, was made. The conditions for observing fluorescence were also unfavorable on account of the light from the spark used to produce ultraviolet rays. Appreciating the weakness of the photo-electric rays, as compared with the kathode rays in an ordinary tube, we had little hope of success in this case also, and did not really give the matter a serious trial.

electrodes L, M and R were held in place by glass tubes which passed through rubber stoppers. These were made air tight by filling the space above with mercury. The figure, being drawn to scale, shows relatively the various dimensions. The distance between K and M was 12 centimeters.

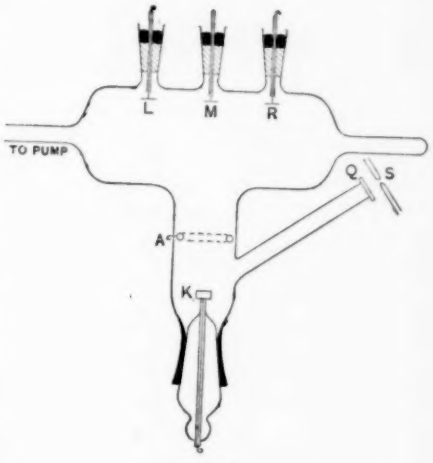

Fig. 1.

In order to admit ultraviolet light into the interior of the tube the quartz plate Q was mounted on the side tube.[1] The end of this tube, which was ground plane, was rubbed with a mixture of tallow and beeswax and the quartz plate laid upon it. After the pump was started this mixture was applied in rather large quantities to the outside of the joint between the tube and the quartz plate. The pressure of the outside air forced the mixture into any small leak due to the imperfect fitting of the plate.

The ultraviolet light that fell on the polished zinc, came through the quartz window, from a spark between zinc terminals. The spark was from two to three millimeters long and was placed two or three centimeters from the quartz window. By suitably arranged screens the ultraviolet light was cut off from all parts of the tube except the zinc kathode, and from all the connecting wires.

The induction coil, condensers, and all connections to the high potential secondary circuit of the coil, including the spark itself, were enclosed in a metallic box, so that the electrodes in the tube were screened from the electrostatic inductive action of the high potential charges. In addition to this the tube itself and the wire leading to the electrometer were surrounded by electrostatic screens. As a further protection to L, M, and R, the tube near the anode was wrapped with a fine mesh wire gauze. When this and the anode

[1] Instead of being in the plane of the figure as shown, this side tube was in a plane perpendicular to the figure and projected toward the observer instead of toward the one side.

were grounded any inductive action of the kathode on the terminals L, M, and R was entirely cut off.

A sensitive Kelvin electrometer, kept at approximately the same degree of sensitiveness by its inductive gauge, was used to determine the potential of the electrode to which it was connected. Usually it was the current passing into the electrode that was wanted. The potential was then observed every five or ten seconds. The difference in successive readings gave the rate of change of potential of the electrode. These values are proportional to the current.

The tube was permanently connected to the vacuum pump. Although the tube had four mercury seals, one ground glass stopper, and the quartz glass joint in addition to the cocks and seals in the pump, it was found that the tube would hold a high vacuum for weeks at a time. No measurements of the pressure in the tube were made, but a rough estimate of the degree of exhaustion was obtained by noting the size of the bubble forced out at each stroke of the pump, and by occasionally observing the character of the discharge produced between L and R by an induction coil. Most of the experiments were performed at a high Crookes' vacuum, but in some cases the pressure was about 1 mm., in which case it could be estimated by a rough gauge.

No attempt was made in any of our experiments to obtain quantitative results. Our intention was merely to show that the properties of the photo-electric rays are qualitatively the same as those of the kathode rays.

MAGNETIC DEFLECTION.

In view of the experiments of Elster and Geitel, Righi, and J. J. Thomson it might at first appear that further evidence of the magnetic deflection of the photo-electric rays is superfluous. It must be remembered, however, that these experiments contain only an indirect proof that the rays are magnetically deflected.[1] The results might be equally well explained in other ways. Thus the experiments of Elster and Geitel showed that the discharge rate was diminished by a strong field. If we assume that the negative ions which carry the discharge are deflected by the field, the results are

[1] Direct proof has been given by Lenard. See foot note p. 230.

satisfactorily explained; but the same result would be produced if the magnetic field, instead of acting on the ions themselves, served merely to so modify the phenomena at the charged surface as to alter the number of ions developed.

In Thomson's experiments an insulated metal plate of practically infinite extent was placed parallel to the charged surface. Upon illuminating the latter the insulated plate received a negative charge. The rate at which this charge was received was found to be diminished by a field parallel to the charged surface, provided the strength of the field exceeded a certain value. The assumption that the photo-electric rays are subject to a magnetic deflection gives an excellent explanation of the effect, since for some critical value of the field strength the rays would be bent through 180° and return to the charged surface.[1] But here too it seems clear that other equally plausible explanations might readily be found.

In fact, both the experiments of Elster and Geitel and those of Thomson are subject to the disadvantages common to all indirect demonstrations. To one who is already inclined to accept the hypothesis upon which they are based, the results are conclusive; but for others they are often far from convincing. For this reason the experiments described below, which afford direct evidence of a magnetic deflection of the photo-electric rays, seem not without interest.

The electrode *M* (Fig. 1) was permanently connected with a quadrant electrometer, and was brought to zero potential by grounding. Upon removing the ground connection and illuminating the zinc kathode by means of the spark at *S* the electrometer showed that *M* was gradually acquiring a negative charge. The rate at which the charge was received depended upon the potential of the kathode, the brilliancy of the spark, and the pressure in the tube. That the

[1] The theory of Thomson's experiment requires that when the critical field strength is reached the transfer of charge to the insulated plate shall entirely cease. In reality the decrease in the rate was found to be quite gradual, and the determination of the critical field strength was attended with considerable uncertainty. It seems clear that the phenomenon is more complicated than the simple theory would lead us to expect. Certainly the discrepancy is sufficiently serious to lead to some question as to the correctness of the conclusions, especially in the mind of one not inclined to regard Thomson's general theory with favor. We shall return to this subject later.

charge was not due to induction, or to any ordinary leakage, was readily proven by a number of obvious tests. It can scarcely be doubted that the charge was carried to M from the kathode chiefly by the photo-electric rays, although reasons will be given later for believing that the effect is complicated to some extent by the ionization of the residual gas. The illumination of the kathode did not serve merely to *start* a discharge, which afterwards continued by itself. The potential of K was far below that necessary to maintain a discharge. Upon preventing the ultra-violet rays from falling upon the kathode the discharge of the latter ceased at once.

A magnetic field at right angles to the line joining Z and M diminished the rate at which M was charged, and if sufficiently strong suppressed it entirely. This diminished rate was *not* due to any falling off in the rate at which the negative electricity was discharged from Z; this was shown by connecting Z to an electroscope and noting the rate at which the latter was discharged, first with, and then without a magnetic field. Doubtless a sufficiently strong field would have diminished the discharge rate, as in the original experiments of Elster and Geitel; but the relatively weak fields employed in our own experiments were unable to produce any measurable diminution.

With a rather weak field, having its positive direction normal to the plane ZLR and directed away from the observer, the charge received by R was *increased* when the field was established, while the charge received by M was diminished. Upon reversing the field its effect upon the charge received by M was the same as before; but the increased charge was now found at L instead of at R. In order that the effect should be sharply marked, it was necessary that the strength of the magnetic field should lie between rather narrow limits. If the field was too weak, the increase in the charge received by R or L was so small as to be scarcely observable; while if the strength of filed was increased beyond its critical value, the charge diminished again, and finally disappeared altogether.

It is clear, from what precedes, that the effect of a magnetic field is to produce a *deflection* of the photo-electric rays; the path followed by the escaping charge is altered, while its amount remains practically unchanged.

The method of taking observations was usually as follows: One of the electrodes, say R, being connected with the electrometer, readings of the latter were recorded every ten seconds so as to obtain the rate of charge. Except with a very strong magnetic field this rate was never zero so long as the kathode was illuminated. Doubtless this fact is explained by the diffuse character of the photo-electric rays; for the form of the apparatus was unfortunately not such as to give a compact beam. After taking enough observations to determine the rate of charge without a magnetic field, the electro-magnet used in developing the field was excited, and the rate was again determined. In some cases the effect of reversing the field was also tested. The results of several sets of observations of this kind are given in Tables I, II, and III. In the first case (I) the strength of field had been adjusted by trial so as to give the maximum effect. It will be observed that the rate at which R was charged was more than doubled by the magnetic field. When the field was reversed (II) a diminished rate resulted. In this case the photo-electric rays were deflected in the opposite direction, and some

TABLE I.

Electrode R. Magnetic field direct (+).

Time after beginning of charge.	Charge rate.	Magnetic field.	Time after beginning of charge.	Charge rate.	Magnetic field.
10 sec.	10	off.	60 sec.	9	off.
20 "	11		70 "	7	
30 "	12		80 "	22	on.
40 "	29	on.	90 "	19	
50 "	29		100 "	8	off.

TABLE II.

Electrode R. Magnetic field reversed (−).

Time after beginning of charge.	Charge rate.	Magnetic field.
10 sec.	14	off.
20 "	6	on.
30 "	7	
40 "	12	off.
50 "	11	
60 "	7	on.
70 "	7	

TABLE III.

Electrode R. Strong field direct (+).

Time after beginning of charge.	Charge rate.	Magnetic field.
10 sec.	16	off.
20 "	2	on.
30 "	17	off.
40 "	2	on.
50 "	15	off.

of the diffuse rays which had previously reached R now no longer did so. Table III gives the results in the case of quite a strong field, whose direction was the same as in Table I. But instead of increasing the rate, it reduced it nearly to zero.

These results appear to us to prove beyond question that the photoelectric rays are magnetically deflected. From the above and other experiments we conclude that when the field is too weak the deflection is small, and the rays proceed to some point between M and R; in this case, while the charge received by M is diminished, that received by R is increased only slightly. Were it not for the fact that the bundle of rays is quite diffuse, it is probable that weak fields would produce no change at all at R. As the field is gradually strengthened the deflection of the rays increases. Finally the deflected rays fall upon the electrode R, and the rate of charge of the latter reaches a maximum. If the field is made still stronger the rays are deflected so far that they pass beyond R, or are intercepted by the walls of the vertical tube. The charge reaching R therefore diminishes again, and finally vanishes.

The relation between the direction of the magnetic field and the direction of the deflection was found to be the same as in the case of the kathode rays. Although no quantitative work was undertaken it was easily seen that the magnitude of the deflection was about the same as would be observed with kathode rays developed in a low vacuum.

It was found that the potential of the zinc kathode was an important factor in determining the susceptibility of the rays to magnetic deflection. When the potential of the kathode was high a much stronger field was required to produce a given deflection than

when the kathode potential was reduced. In other words the photo-electric rays became "stiffer" as the potential of the kathode was increased. The same is true with the ordinary kathode rays. The photo-electric rays were deflected much more readily than the kathode rays in an ordinary X-ray tube. It is to be remembered that the potential of the zinc kathode was only slightly in excess of 1000 volts.

The deflection was only slightly affected by changes in pressure. In this respect the photo-electric rays would appear at first glance to differ essentially from the kathode rays; for it is well known that by altering the pressure in a vacuum tube we may change the magnetic deflection of the kathode rays very greatly. But it must be remembered that in such cases the change in the magnetic deflection is really a secondary effect. The first effect of altering the pressure is to change the potential difference necessary to produce discharge, and since the magnetic deflectability of the rays is completely determined by the fall of potential in the tube[1] a change in their stiffness necessarily follows.

In addition to the photo-electric rays proper, in which the charged particles are probably identical with those which form the kathode rays, it appears to us that heavier and more sluggish ions are also present, whose motion is practically unaffected by a magnetic field. The experiments leading to this view, which unfortunately give only indirect evidence of its correctness, were as follows:

Having determined the rate at which M was charged in the absence of a magnetic field, the rate was redetermined with a field sufficiently strong to deflect the rays far beyond R. The latter rate was still far from zero. In one instance, when the pressure in the tube was about 1 mm, the ratio of the two rates was 4.3 : 1. Upon carrying the exhaustion further this ratio was found to steadily increase, and in the set of observations just mentioned it finally reached a value of 8.2 : 1.

It is quite possible that these results might be accounted for by the extreme diffuseness of the photo-electric rays, since the diffusion would naturally be less at high exhaustions. We know,

[1] Kaufmann, Wied. Ann. 61, p. 545, 1897; J. J. Thomson, Phil. Mag. 44, p. 193, 1897.

however, from the experiments described in the next section, that the residual gas in the tube is ionized by the photo-electric rays. Ordinary gaseous ions are therefore present in practically all parts of the tube. We are inclined to ascribe the results just mentioned in part at least to the presence of these ions, rather than to a scattering of the photo-electric rays. Under the influence of the electric field between A and K the negative ions developed in that region will move in the same general direction as the photo-electric rays; but since these ions are not produced at the kathode itself, but throughout the whole region traversed by the photo-electric rays, the direction of their motion need not be even approximately normal to the kathode surface. While most of the negative ions doubtless fall upon the anode and there give up their charge, some will probably pass beyond A. In the region above A two kinds of negative particles are therefore present: (1) the small rapidly moving corpuscles of the photo-electric rays, forming a fairly compact stream normal to the kathode; (2) the relatively heavy and slowly moving negative ions, which form a stream having the same general direction as the photo-electric rays but much more diffuse. The photo-electric rays are deflected by a magnet; the moving ions on the other hand, on account of their greater inertia, are not appreciably affected by magnetic influences.[1]

The view here advanced not only gives a satisfactory explanation of our own results, but also explains the partial discrepancy between experiment and theory in the experiments of Thomson.[2]

IONIZATION.

As is now well known, kathode rays in passing through any gas make it for the time being a conductor. Following the ordinary electrolytic hypothesis, it is thought that under the impact of kathode rays some of the molecules are broken up into ions. Part of these ions carry positive, while the rest carry negative

[1] As the ionization produced by photo-electric rays has not been previously investigated, the assumption that the ions possess relatively large inertia rests only on analogy with other instances of gaseous conduction. In all cases so far studied there is every reason to believe that the ions produced are much larger than the kathode ray corpuscles. It is natural to suppose that the same is true in this case.

[2] See foot-note p. 235.

charges, the result being that a temporary power of electrical conduction is imparted to the gas. If the photo-electric rays are identical in character with kathode rays, the gas through which this discharge passes should become conducting. We were able to show that this was the case in several different ways.

The electrode *M*, Figure 1, lies directly in the path of the negatively charged particles that compose the photo-electric stream. As these particles impinge on *M* they give to it a negative charge. *M* will therefore accumulate a negative charge, and, if the gas were not a conductor, the potential of *M* would increase until the electrical repulsion prevented more negative particles from approaching *M*. This potential would have to be high, as the ions from *K* approach *M* with considerable velocity. Observation shows, however, that *M* instead of reaching a high potential under the impact of the rays becomes charged to a potential of only a few volts. The simplest explanation of this is that the photo-electric rays ionize the gas. As soon as *M* becomes charged negatively it attracts the positive ions. The final potential reached by *M* represents the state of equilibrium between the inrush of the negative corpuscles of the photo-electric rays and of positive ions from the surrounding gas.

If one of the side electrodes, say *L*, was charged by a dry pile while *M* connected to the electrometer, a current passed through the gas between *M* and *L*. The direction of this current could be reversed by changing the sign of the charge on *L*. To eliminate errors due to the inductive effect of charges that may accumulate on the glass walls of the tube or to charges in the gas itself, the electrodes, *L*, *M*, and *R* were incased in metallic cylinders. In the final experiments the electrode, *M* was built in slightly different form from the others, so that a high potential difference could be maintained between the cylinder *B* and the electrode *M* (Fig. 2) without an appreciable leakage. The electrode *M* was an aluminium wire supported by the glass tube *ab*, and was permanently connected to the electrometer. The cylinder *B* was held in place by the polished ebonite block *e*. The glass tube *ab* passed through the rubber stopper *d* and the mercury seal *c*. Being connected by a small wire to *R*, Fig. 1, the cylinder could be charged to any desired potential.

The usual method of observing the current between *B* and *M*

was to first ground the electrometer and then, having insulated it, to note the rate of change of the potential of M. This rate is proportional to the current going through the gas to M. When B was charged positively, M took a positive charge; when B was negative, a negative charge was given to M. That this conductivity was due to the passage of the photo-electric rays through the gas was easily shown. The vacuum was so high that for the potentials used it was a perfect insulator. It was only when the photo-electric rays passed near B that the conduction occurred. Screening off the ultraviolet light, or removing the negative charge from the zinc, stopped the effect. When a magnet deflected the rays from K against the walls of the tube near K the conductivity was destroyed and no current passed from B to M. Upon removing of the magnet, current again flowed. Anything that stopped the photo-electric rays destroyed the conductivity.

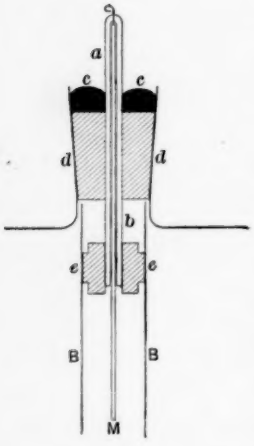

Fig. 2.

In observing the current between the wire M and the cylinder B, the latter being charged positively, rather striking effects were noticed, both when the ultraviolet light was first allowed to fall on the kathode, and when the light was screened off. The current instead of gradually increasing to a maximum started in the reversed direction with a rather large value, then slowly decreased to zero and reversed.

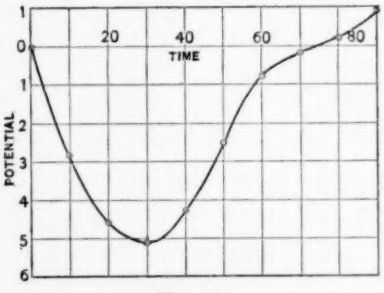

Fig. 3.

Figure 3 shows graphically the change in potential of the electrode M.[1] Time in seconds is counted from the instant the ultraviolet light is started. In this case the ground connection of the electrode M was broken before the spark producing the ultraviolet light was started.

[1] The slope of the curve at any point is proportional to the current at that instant.

In explaining this effect it must be remembered that the process of ionizing a gas is not an instantaneous one. As soon as an ion is created it comes at once under the influence of the electrostatic field, moves over to one of the conductors and is destroyed. For some time the ions are generated by the rays faster than they are thus destroyed. Therefore during this time the number of ions is increasing. The first rush of negatively charged corpuscles in the photo-electric rays imparts a negative charge to the electrode *M*, and until the time when the number of positive ions reaching *M* exceeds the number of negative corpuscles the current will flow in the negative direction.

When the stream of particles from the kathode was cut off the current was for a short time greatly increased. This was true only when *B* was charged positively and when the electrometer was taking a positive charge. As has already been shown the current measured is the result of two opposing currents, one due to the negative charges brought by the photo-electric rays, and the other to the positive ions moving under the electrostatic forces. Therefore, if one is suppressed, as in this case the negative ions, the resultant is increased. The effect was the same whether the rays were stopped by breaking the current in the induction coil that furnishes the spark giving the ultraviolet light, or by screening off the ultraviolet light, or by deflecting the rays with a magnet.

In Figure 4 is shown graphically the effect on the change of potential of *M*, both of starting and stopping the ultraviolet light.

It will be noticed in the curve that the electrode *M* continued taking a positive charge for about thirty seconds after the spark was stopped. This can hardly be due entirely to the positive ions left in the gas, as they probably move too rapidly to last longer than a few seconds. The complete explanation of this phenomenon is not clear to us.

When *B* is negative, negative ions under the electrostatic forces go from the gas to *M*. There is therefore no tendency to oppose the effect of the negative corpuscles of the rays which impinge on *M* as is the case when *B* is positive. Hence no reversal of the current is found after the rays are started. When the ultraviolet light is suppressed the current died down to zero in a few seconds.

It was found for high vacua that the conductivity decreases as the pressure of the gas in the tube decreases. This is to be expected, since it is known that the amount of ionization imparted to a gas depends among other things upon the absorption of the rays by the gas. As the vacuum is increased the absorption decreases and the number of ions present is diminished. This decreased conduc-

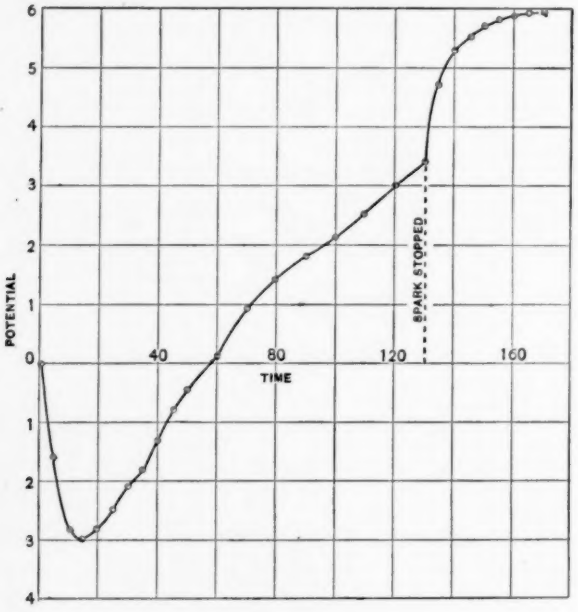

Fig. 4.

tivity is easily shown by observing the permanent deflection acquired by the electrode M while B was grounded. This depends, as has been previously explained, on the conductivity of the air as well as on the intensity of the photo-electric rays. When the pressure of the gas was decreased the potential acquired under the impact of the photo-electric rays was increased.

ELECTROSTATIC EFFECTS.

Since the residual gas is rendered conducting by the photo-electric rays, the direct proof of an electrostatic deflection of these rays is subject to considerable experimental difficulty. The difficulty is in fact the same as that which so long concealed the

existence of the corresponding phenomenon in the case of the kathode rays. For this reason we had not intended to undertake a study of the electrostatic properties of the rays without apparatus especially constructed for the purpose. But indirect evidence of electrostatic deflection was accidentally obtained which is not without interest.

In the course of our experiments upon the conducting power imparted to the air by the photo-electric rays, numerous observations were made to determine the relation between the difference of potential between B and M and the current flowing. In all other cases of electrolytic conduction in gases it has been observed that Ohm's law does not hold, but that with increasing electromotive force the current approaches a limiting value; in other words the current becomes "saturated." In the present case the phenomenon

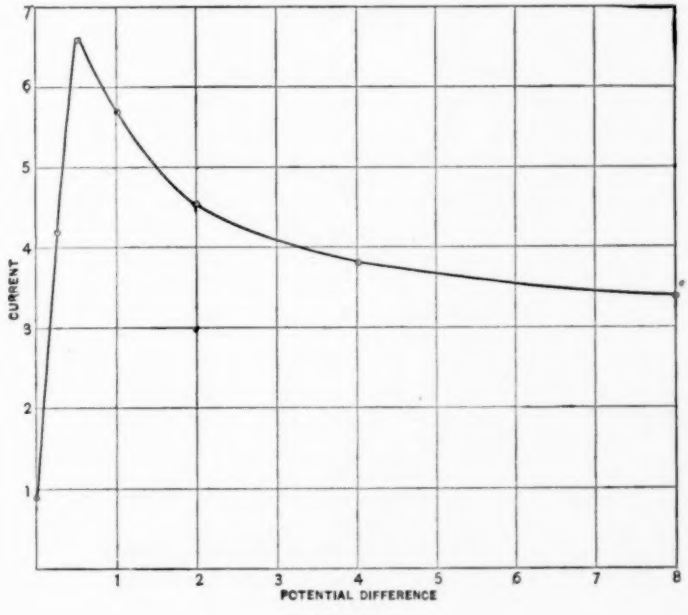

Fig. 5.

is more complicated, and the results obtained seemed at first difficult of explanation.

With the cylinder B (Fig. 2) charged to different potentials, the current passing between B and M was determined as in the experi-

ments described in the last section. It was found that as the potential increased the current at first increased nearly in the same ratio. Indications of approaching saturation were however soon noticed, and when a potential of about 100 volts was reached, the current had attained its maximum value. If B was charged negatively a further increase in the potential difference caused a *diminution* in the current. For a potential difference of about 100 volts the current was nearly twice as great as for a potential difference of 1,000 volts. The results are shown graphically in Fig. 5.

When B was positive this peculiar behavior was not observed, and the saturation curve was found to have the usual form.

It appears to us that the results observed when B was negative are due to the electrostatic repulsion between the charged cylinder and the negative particles of the photo-electric rays. When the potential of the cylinder attains a value that is at all comparable with the potential of the kathode, this repulsion either deflects the rays, so as to produce a decrease in the number of particles passing near B, or reduces the speed of the particles. In either case the ionization in the region near B and M would be diminished, and the current between them might become less, in spite of the increased

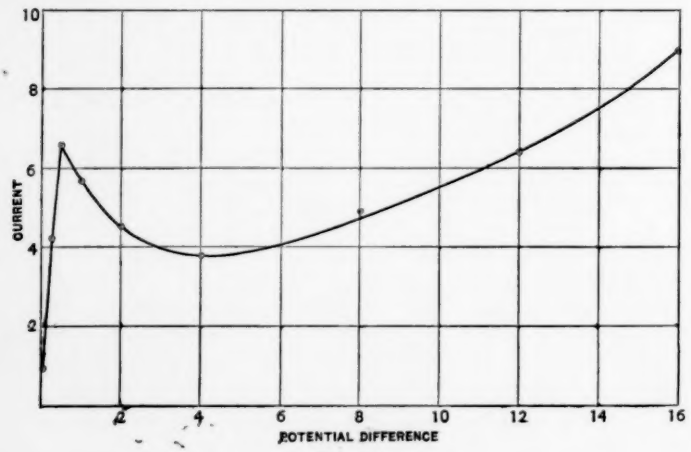

Fig. 6.

potential difference. Except for the low potential of the kathode, which was rarely above 1,000 volts, the effect would probably have been inappreciable.

It appeared interesting to determine what would happen if the cylinder B was made more strongly negative than the kathode. In this case it would clearly be impossible for particles which owed their motion to repulsion from K, to proceed as far as B. At first thought we should therefore expect the current between B and M to fall to zero. Instead of this the saturation curve took the form shown in Fig. 6. The potential of the kathode in these experiments was, as usual, about 1,000 volts. Two considerations not mentioned in the preceding paragraph appear sufficient to explain these results. First, it seems probable that the current between B and M is not carried solely by the ions that are developed in the

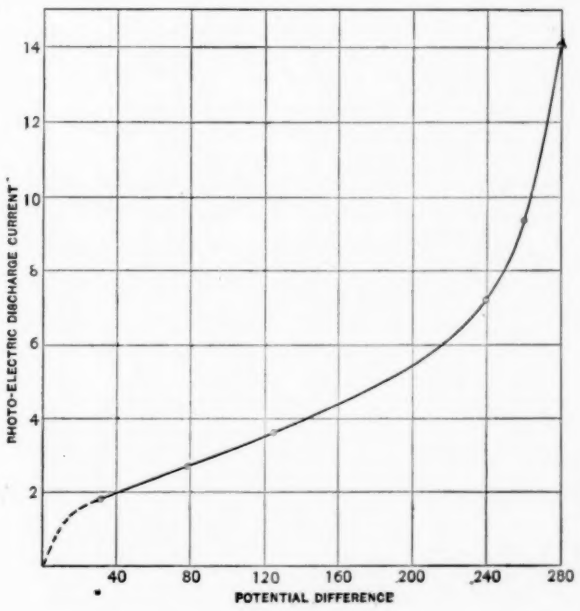

Fig. 7.

region immediately between the two, but that ions produced at a distance from B may also take part in the conduction. This might result in part from a slow diffusion of the ions, although the effect of a magnetic field in suppressing the current shows that the diffusion is quite small. The field due to the charge on B extends, however, throughout the whole of the region above A. It seems not unlikely that some of the lines of force

extending from B to M may pass through a region where ionization has occurred. In this case a current would flow, even if the space immediately surrounding M was absolutely non-conducting. The fact that the current not only does not vanish for high negative potentials, but actually increases, is probably related with the phenomena observed by Kreusler[1] and v. Schweidler,[2] who found that for potentials approaching that of normal discharge the photo-electric current increased with great rapidity. In Fig. 7 we reproduce one of the curves given by v. Schweidler. The air pressure in this case was about 17 mm. The results of Kreusler and v. Schweidler, together with those obtained in our own experiments, appear to us to indicate that when a gas is subjected to strong electric stress its susceptibility to the ionizing action of the photo-electric rays is greatly increased.

DISCUSSION AND THEORY.

The preceding experiments show that the photo-electric rays, like kathode rays, are deflected in passing through a magnetic field; that they render the air through which they pass conducting; and that in all probability they are deflected by electrostatic forces. That they carry a negative charge has long been known. The experiments of Thomson[3] and Lenard[4] show that the ratio e/m is the same, within experimental errors, as in the case of ordinary kathode rays. The fact that we have not yet been able to detect any fluorescence produced by the photo-electric rays is readily accounted for by the small intensity of the rays used in these experiments; and their failure to produce Röntgen rays is doubtless due to a similar cause.

In view of these facts the conclusion seems to us warranted that the photo-electric rays are identical in character with ordinary kathode rays.

The mechanism of the process by which the photo-electric rays are produced is still far from clear. It is not even known whether

[1] Über den photo-elektrischen Effect in der Nähe des Entladungpotentiales, Verh. der phys. Ges., Berlin, Vol. 17, No. 8.

[2] Sitzungsberichte der k. Akad. zu Wien., 108, IIa, p. 273, 1899.

[3] Phil. Mag. 48, p. 547.

[4] Annalen der Physik, Vol. 2, p. 359. 1900. § 3.

they come from the material of the charged body itself or from the layer of gas at the surface. In the theory of the the photo-electric discharge advanced by Elster and Geitel [5] the rays are assumed to originate in the gaseous layer. Lenard, on the other hand, having found that photo-electric rays are developed even at the highest vacuum attainable, is of the opinion that the effect is independent of the presence of air ; in this case the material of the kathode is the only remaining source. It does not appear to us that Lenard's results are conclusive on this point; for although he probably worked with a vacuum as nearly perfect as any that has ever been obtained, yet an *absolute* vacuum is of course out of the question. Again, it is known that there is a tendency for a layer of gas to form over a metallic surface which the most persistent pumping and heating fail to entirely remove. We are, therefore, of the opinion that the source of the corpuscles that form the photo-electric rays must still be regarded as unknown. It may be mentioned in passing that the same uncertainty exists in the case of ordinary kathode rays.

Although there appears to be little doubt that real kathode rays may be developed, at sufficiently low pressure, merely by illuminating a suitable surface with ultra-violet light, there is no experimental evidence that the rays can be developed in this way at atmospheric pressure. Yet the photo-electric discharge occurs at atmospheric pressure as well as in a vacuum. There are important differences between the two cases ; but it appears to us that the phenomenon must be essentially the same in both. The following way of looking at the matter seems to us sufficiently plausible to deserve consideration.

We assume first that the primary effect of illumination is to cause the development of kathode rays, and that these rays are produced not only at low pressures, where it has been possible to detect them directly, but also under ordinary atmospheric conditions. Remembering that the rays make the air a conductor, it is seen that the photo-electric current will in general consist of two parts : (1) the current carried by the photo-electric rays themselves ; (2) the current carried by the ionized air. At high vacua practically the whole current will be carried by the photo-electric rays. But as the pres-

[5] Wiedemann's Annalen 55, p. 697.

sure of the surrounding air increases, the rays will be more and more completely absorbed, and since this absorption results in ionization, the conduction current through the air will become more important. At atmospheric pressures the rays are probably absorbed in the immediate neighborhood of the charged surface. In this case the discharge is almost wholly carried by electrolytic conduction; but since the ions are developed very close to the surface the case differs essentially from that of the ionization produced in gases by other causes. In most cases both positive and negative ions are present throughout the gas. But in the photo-electric discharge the positive ions pass at once to the kathode and are destroyed.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY.

A NEW METHOD OF MEASURING THE RESISTANCE OF A GALVANOMETER.

By Wm. S. Day.

THE following method of measuring the resistance of a galvanometer I have not seen described before, although it has very likely occurred to others. It is not always more accurate nor more convenient than other methods, but as it could be used with a supply of apparatus which would not allow of using the usual other methods, it may be worth putting on record. It might also be of use as a laboratory experiment for students.

The method is based on the simple notion that if the terminals of a galvanometer are brought to a certain potential difference, and the resulting current through the galvanometer gives a certain constant deflection, when the needle comes to rest, then, if we double this potential difference, in order to keep the same current through the galvanometer and the same deflection, it will be necessary to double the resistance of the galvanometer circuit by adding a resistance equal to that of the galvanometer. In order to be able to double the potential difference, use may conveniently be made of the uniform fall of potential along a wire of uniform resistance per unit length, such as the wire of a Wheatstone wire bridge, when it is carrying a constant current. The galvanometer terminals may be placed in contact with points on such a wire a suitable distance apart, and the constant deflection noted. This distance may then be doubled and at the same time a resistance may be inserted in series with the galvanometer and varied until the deflection becomes the same as at first. Then supposing the resistance of the part of the bridge wire between the terminals is negligible in comparison with the galvanometer resistance, the resistance inserted will be the same as that of the galvanometer. If, however, it would not be proper to overlook the resistance of this portion of the wire in comparison with the galvanometer resistance, its effect may be allowed for by taking a third position of the terminals three times as far apart on the bridge wire as their original position, and observing what resistance is then necessary to keep the galvanometer current the same. The manner of doing this will be shown presently. Of course, it is not even necessary and sometimes may be impossible to double and treble exactly the distance apart of the points of contact. The formula covering this more

general case from which the simple cases follow, can be deduced by writing down the condition that the current through the galvanometer, each time the contact is made, is the same. The diagram represents the state of affairs. There is a battery cell, a suitable but not necessarily known resistance, and a bridge wire, in series. The two galvanometer wires make contact with the points P and Q_1, in the first part of the experiment. The dotted lines represent the arrangement of the galvanometer wires in the second and third parts of the experiment, in which while one terminal is kept at P, the other one makes contact successively at the points Q_2 and Q_3. The notation is

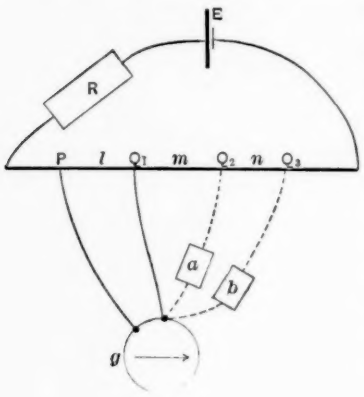

Fig. 1.

E = the electromotive force of the battery, supposed constant.

R = the whole resistance of the battery circuit up to the extreme points P and Q_3 at which contact is made.

ρ = the resistance of the bridge wire per unit length.

l = the length of the segment of the wire PQ_1.

m = the length of the segment of the wire Q_1Q_2.

n = the length of the segment of the wire Q_2Q_3.

g = the galvanometer resistance.

a = the resistance added to the galvanometer circuit when the terminals are at P and Q_2.

b = the resistance added when they are at P and Q_3.

In addition let

C = the constant current through the galvanometer.

C_1, C_2, C_3 = the currents in the three cases flowing through the main battery circuit. The current through the battery circuit in the three cases will be given by the three expressions

$$C_1 = \frac{E}{R + (m+n)\rho + \dfrac{\rho l g}{\rho l + g}}$$

$$C_2 = \frac{E}{R + n\rho + \dfrac{\rho(l+m)(g+a)}{\rho(l+m) + g + a}}$$

$$C_3 = \frac{E}{R + \dfrac{\rho(l+m+n)(g+b)}{\rho(l+m+n) + g + b}}.$$

The galvanometer current will be the fractional part of these currents represented by the equations

$$C = \frac{\rho l}{\rho l + g} C_1 = \frac{\rho(l+m)}{\rho(l+m)+g+a} C_2 = \frac{\rho(l+m+n)}{\rho(l+m+n)+g+b} C_3 .$$

Substituting in these the expressions for C_1, C_2 and C_3 we get the following two equations:

$$\frac{\rho l E}{(\rho l + g)[R + (m+n)\rho] + \rho l g}$$

$$= \frac{\rho(l+m)E}{[\rho(l+m)+g+a](R+n\rho)+\rho(l+m)(g+a)}$$

$$= \frac{\rho(l+m+n)E}{[\rho(l+m+n)+g+b]R+\rho(l+m+n)(g+b)} .$$

It will be seen that the factor ρE can be divided out at once and on eliminating R it will be found that ρ appears merely as a factor. Dividing it out and solving for g we get the expression

$$g = \frac{l[(l+m+n)(m+n)a - m(l+m)b]}{mn(m+n)} \qquad (1)$$

which gives g in terms of the measurable quantities.

If in (1) $l = m = n$, the equation is reduced to the simple form

$$g = 3a - b. \qquad (2)$$

If ρl were negligible in comparison with g it would not be necessary to find the resistance b, and the equation would be

$$g = \frac{l}{m} a. \qquad (3)$$

Or, if $l = m$,

$$g = a \qquad (4)$$

So far as the formulæ show there does not appear to be any reason why the method could not be used with galvanometers of any resistance or of any sensitiveness. With sensitive galvanometers, however, thermo-electric effects may give irregular deflections, although these are fully as troublesome in using Lord Kelvin's method. To avoid them as much as possible, care must be taken to touch the wires and connections with the warm hand as little as possible. The chief difficulty to be met with in applying the method to sensitive d'Arsonval galvanometers using a phosphor bronze suspension ribbon is the tendency for the zero to change owing perhaps to elastic fatigue or variation of some kind of the suspend-

ing wire. This can be partly avoided by taking the readings quickly and always observing the actual zero point before each deflection is taken. The method was applied to the following five galvanometers, whose resistances are given and the number of the formula applied:

1.	D'Arsonal, made by Queen & Co.	1097.	ohms.	(4)
2.	Rowland d'Arsonval, made by Willyoung.	1204.	"	(4)
3.	Astatic galvanoscope, made by T. W. Gleeson.	10.39	"	(1)
4.	" " " L. E. Knott.	0.86	"	(1)
5.	Voltmeter (without multiplier) Weston.	1.08	"	(1)

The resistance of each of these instruments as given was measured with the help of another galvanometer by the ordinary Wheatstone bridge method, the temperature of the room being observed at the same time. After making a number of trials so as to discover the source of the errors likely to arise and the precautions necessary to avoid them, it was found possible to measure the resistances by the new method described, within 2 per cent. or 3 per cent. Kelvin's method[1] seemed less accurate than this for the Queen instrument, and about the same for the Rowland and Weston instruments. The Queen instrument gave a deflection of 1 millimeter on a scale 1 meter distant, for a current of about 1.5×10^{-9} amperes. The Rowland instrument required about four times as much current for an equivalent deflection. The wire used for the measurements was one on a cheap form of Wheatstone wire bridge for students' use. It was 1 meter long, and had a resistance of about 6.5 ohms. As any piece of uniform wire stretched on a board could be used, the only other piece of apparatus necessary beside the battery would be a resistance box, and a few pieces of wire. Lord Kelvin's method could not easily be used with such a supply of apparatus.

The unknown contact resistances where the galvanometer terminals are placed in contact with the wire, may become an important cause of error in measuring a very low resistance galvanometer.

[1] Maxwell, Elect. and Mag., 3d ed., vol. 1, p. 489.

THE VERIFICATION OF BOYLE'S LAW.

By N. H. Williams.

THE value of the experimental verification of Boyle's law as a laboratory exercise in elementary physics is unquestioned. It is usually the first inverse relationship that the student meets in his experimental work; it furnishes him a new study in the representing of relations by curves, and is on the whole one of the most valuable experiments in the elementary course.

The apparatus that has usually been employed for this experiment needs no description. It is acknowledged to have some defects, among which might be mentioned the stretching of the rubber tube connecting the two glass tubes. This usually causes considerable error in the work. The size, usually two metres long, is another objection to it, as is also the expense if many pieces are needed.

With the old type of apparatus, the rubber tube soon deteriorates, a leak develops, and several pounds of mercury are lost.

These are a few of the reasons why an effort has been made to improve the apparatus for this experiment.

In the figure *D* represents a small glass bottle with a wide mouth fitted with a rubber stopper. Two glass tubes about an eighth of an inch in internal diameter pass through the stopper and dip into the mercury in the bottle. The tubes are about eighteen and thirty inches in length respectively. The short one is closed at the upper end by fusing a glass plug into it. If this seems difficult to do, a little wax melted in over the plug will make it perfectly tight without fusing. This gives a square cut end from which to measure the length of the air column. The amount of air in the tube is adjusted by placing the apparatus in a horizontal position and allowing mercury to run into the tube till a column of air about 20 cms. in length remains.

V is a bicycle valve, which passes through a third hole in the stopper. The valve and the tubes are moistened with liquid glue before they are inserted. The stopper is also glued into the bottle.

When the apparatus is ready for use, a bicycle pump is employed to produce a pressure in the bottle sufficient to force the mercury nearly to the top of the long tube.

The apparatus is then placed before the mirrored scale of a Jolly balance, and the positions of *A*, *B*, and *C* accurately read. A little air is

then allowed to escape from the bottle for the purpose of varying the pressure, and another set of readings is taken. This operation is repeated until ten or fifteen sets of readings have been taken.

$C = 18.00$ *Barometric reading* 74.20 *c. m.*

B	A	$B-A$	P	V	PV
30.43	13.40	17.03	91.23	12.43	1134
31.00	17.90	13.10	87.30	13.00	1135
31.55	21.90	9.65	83.85	13.55	1136
32.10	25.80	6.30	80.50	14.10	1135
32.63	29.15	3.48	77.68	14.63	1136
33.34	33.45	− 0.11	74.09	15.34	1136
34.02	37.11	− 3.09	71.11	16.02	1139
34.73	40.90	− 6.17	68.03	16.73	1138
35.39	44.00	− 8.64	65.59	17.39	1141
35.98	46.70	−10.72	63.48	17.98	1141
36.70	49.70	−13.20	61.00	18.70	1141

The difference, $B - C$, is taken as the volume of the confined gas, and the pressure is found by adding the barometric reading to the difference $B - A$. This difference becomes negative as A falls below B, thus giving pressures less than atmospheric.

The last column consists of the products of the volumes by the corresponding pressures. It shows an extreme variation of a trifle over one-half of one per cent.

It will be seen at once that this apparatus possesses advantages over the other. It is small and light, is inexpensive and easily made. The mercury does not come in contact with rubber. Errors due to the stretching of rubber are avoided and the results are considerably better than those usually obtained by the other apparatus.

The gradual increase in the products with decreasing pressure is an error due largely to the presence of moisture in the enclosed gas.

CENTRAL HIGH SCHOOL, DETROIT, June 16, 1900.